

Fractional Coverage Model for the Adsorption and Removal of Gas Species and Application to Superlow Friction Diamond-Like Carbon

P. L. Dickrell

W. G. Sawyer

University of Florida,
Mechanical Engineering Department,
Gainesville, FL 32611, USA

A. Erdemir

Argonne National Laboratory,
Energy Technology Division,
Argonne, IL 60439, USA

The frictional behavior of diamond-like carbon (DLC) films varies with environmental condition. One theory asserts that the cause of variations in the frictional performance is environmental contaminants adsorbing onto the DLC film surface. Testing of the frictional performance of DLC films in a pin-on-disk contact has mapped the transient behavior of the friction coefficient. A model for fractional coverage, based on the adsorption of environmental contaminants and their removal through the pin contact, is developed. The rate of adsorption is taken from Langmuir's model [17], which is combined with the removal ratio from Blanchet and Sawyer [18]. The coefficient of friction is based on the average fractional coverage under the pin contact. The model also gives a closed-form expression for the steady-state fractional coverage. Model calculations compared favorably to the time progression of the friction coefficient for a series of earlier experiments on a superlow friction DLC coating [7], when the fractional removal term was allowed to increase with increasing sliding speed. [DOI: 10.1115/1.1739408]

Introduction

The unique properties of diamond-like carbon (DLC) films are characterized by excellent wear resistance, biocompatibility, and chemical inertness. These films can potentially be used in a wide range of applications, such as bearings, cutting tools, submersible parts, and biomedical applications [1–4]. Testing of DLC films as solid lubricant coatings has shown them to possess low coefficients of friction, spanning the range $\mu=0.001$ to 0.6 [3–6], although the testing conditions and type of DLC film (i.e., hydrogenated versus hydrogen-free) have a strong influence on its frictional behavior. The frictional behavior of the superlow friction DLC film, recently investigated at Argonne National Laboratory [4,7], has been theorized to be dependent on the amount of contaminants adsorbed on the rubbing surface [7].

Some attempts have been made to model the frictional behavior of DLC and other carbon films in various environments [3,8,9]. A hypothesis is that the variations in friction coefficient with sliding speed in a pin-on-disk contact are the result of competitive rate processes that involve an interaction of a contaminant gas species with the surface of the diamond-like carbon, such as the adsorption of water, and the removal of these species under the contact of the pin. Much like vapor-phase lubrication [10–16], such processes have a strong dependence on the gas pressures of the contaminants, available areas for adsorption, time exposed to the environment, and temperature. This paper outlines the development of a closed-form, time-dependent model for such competitive processes using, principally, the works of Langmuir [17] and Blanchet and others [10–16,18]. Such a model may be useful for gaining fundamental understanding of the frictional behavior of these and other surfaces that show a strong dependence on the environment.

In a model presented by Heimberg et al. [7] the Elovitch model was used with a linear rule-of-mixtures in friction coefficient to

give a closed form expression to describe the increasing friction coefficient with increasing exposure times. This model was developed without a removal term, and, therefore, could not predict any steady-state behavior. In the model developed here a removal term wipes away a fraction of the adsorbed species each cycle, and thus is capable of not only predicting transient behaviors but also predicting a partially covered steady state.

Modeling

The model assumes some initial surface fractional coverage θ_0 of an adsorbed species. At time equals zero, or the initiation of an experiment, this term is the fractional coverage that enters into the initial pin contact. The fractional coverage that then leaves the contact θ_{out} is assumed to be less than the entering fractional coverage for two reasons (1) adsorption of gaseous species is assumed to be negligible under the pin contact, and (2) removal of adsorbed species is assumed to occur under the pin contact as a combination of mechanical removal and thermal desorption as a result of frictional heating. After the surface element leaves contact, it is exposed to the gaseous environment, and adsorption occurs on the surface during the time it takes for the surface element to return to contact. The subsequent entering fractional coverage θ_{in} varies from cycle to cycle until the system reaches equilibrium.

This model follows the works of Langmuir [17] and Blanchet and Sawyer [18] for the adsorption and removal of fractional films, respectively. Following Langmuir, the adsorption of a gas species occurs on the fraction of the surface that is not covered, $(1-\theta_{out})$, in the time from when the surface exits the pin contact to when it enters the pin contact on the next revolution. The adsorption ratio, α , is the fraction of the uncovered surface coming out of the pin contact that becomes covered by an adsorbed species between cycles. If the time between contacts, temperature, and gaseous environment remain constant, the adsorption ratio α will not change between cycles, although the fractional coverage will. Following Blanchet and Sawyer, the removal ratio, λ , is the ratio of the fraction of the surface covered at the exit of the pin

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Table 1 Analytical expressions for the entering fractional coverage for the first few cycles

θ_{0in}	$= \theta_0$	$= \theta_0$
θ_{0out}	$= \lambda \theta_0$	$= \lambda \theta_0$
θ_{1in}	$= \theta_{0out} + (1 - \theta_{0out})\alpha$	$= \lambda \theta_0 + \alpha - \lambda \alpha \theta_0$
θ_{1out}	$= \lambda \theta_{1in}$	$= \lambda(\lambda \theta_0 + \alpha - \lambda \alpha \theta_0)$
θ_{2in}	$= \theta_{1out} + (1 - \theta_{1out})\alpha$	$= \lambda^2 \theta_0 + \lambda \alpha - 2\lambda^2 \alpha \theta_0 + \alpha - \lambda \alpha^2 + \lambda^2 \alpha^2 \theta_0$
θ_{2out}	$= \lambda \theta_{2in}$	$= \lambda(\lambda^2 \theta_0 + \lambda \alpha - 2\lambda^2 \alpha \theta_0 + \alpha - \lambda \alpha^2 + \lambda^2 \alpha^2 \theta_0)$
θ_{3in}	$= \theta_{2out} + (1 - \theta_{2out})\alpha$	$= \lambda^3 \theta_0 + \lambda^2 \alpha - 3\lambda^3 \alpha \theta_0 + \lambda \alpha - 2\lambda^2 \alpha^2 + 3\lambda^3 \alpha^2 \theta_0 + \alpha - \lambda \alpha^2 + \lambda^2 \alpha^3 - \lambda^3 \alpha^3 \theta_0$
θ_{3out}	$= \lambda \theta_{3in}$	$= \lambda(\lambda^3 \theta_0 + \lambda^2 \alpha - 3\lambda^3 \alpha \theta_0 + \lambda \alpha - 2\lambda^2 \alpha^2 + 3\lambda^3 \alpha^2 \theta_0 + \alpha - \lambda \alpha^2 + \lambda^2 \alpha^3 - \lambda^3 \alpha^3 \theta_0)$

contact to that at the entrance. This fractional removal of the adsorbed species occurs differentially through the pin contact and is ensured to be between 0 and 1. An expression for the average fractional coverage under the pin is used to make friction coefficient predictions.

This model is recursive, and application of the equations gives a fractional coverage sequence for the first few cycles, as shown in Table 1. No pattern quickly emerges from this sequence. However, the pattern is obvious if one looks at the difference between the entering fractional coverage for each cycle and that of the previous cycle. In Table 2, N is the cycle number, and the difference in fractional coverage is defined as $\Delta \theta_N = \theta_N - \theta_{(N-1)}$.

Thus, the equation for the coverage going into the pin contact at any cycle n is the initial coverage plus the sum of the differences up to cycle n , as shown in Eq. (1).

$$\theta_{n,in} = \theta_0 + \left(\sum_{N=1}^n \lambda^{(N-1)} (1-\alpha)^{(N-1)} \right) (\lambda \theta_0 + \alpha - \lambda \alpha \theta_0 - \theta_0) \quad (1)$$

Quite fortuitously this series has a closed-form expression, given in Eq. (2).

$$\sum_{N=1}^n \lambda^{(N-1)} (1-\alpha)^{(N-1)} = \frac{1 - (\lambda(1-\alpha))^n}{1 - \lambda + \alpha \lambda} \quad (2)$$

The cycle-dependent entering fractional coverage at any cycle n can then be compactly written as given in Eq. (3).

$$\theta_{in} = \theta_0 (\lambda(1-\alpha))^n + \alpha \left(\frac{1 - \lambda^n (1-\alpha)^n}{1 - \lambda(1-\alpha)} \right) \quad (3)$$

The steady-state solution for the entering fractional coverage can be determined by taking the limit of this function as the number of cycles approaches infinity, given by Eq. (4).

$$\theta_{ss,in} = \frac{\alpha}{1 - (1-\alpha)\lambda} \quad (4)$$

This expression agrees with steady-state expressions developed previously by Sawyer and Blanchet [10]. The adsorption ratio α can be found from the Langmuir solution for vapor adsorption, which states that the rate of adsorption is a product of the adsorption coefficient (ν), the gas pressure (P), and the nascent surface area fraction ($1 - \theta$).

$$\frac{d\theta}{dt} = \nu P (1 - \theta) \quad (5)$$

Table 2 Analytical expressions for the difference between the entering fractional coverage for the first few cycles

$\Delta \theta_1$	$= \lambda \theta_0 + \alpha - \lambda \alpha \theta_0 - \theta_0$
$\Delta \theta_2$	$= \lambda(1-\alpha)(\lambda \theta_0 + \alpha - \lambda \alpha \theta_0 - \theta_0)$
$\Delta \theta_3$	$= \lambda^2(1-\alpha)^2(\lambda \theta_0 + \alpha - \lambda \alpha \theta_0 - \theta_0)$
$\Delta \theta_4$	$= \lambda^3(1-\alpha)^3(\lambda \theta_0 + \alpha - \lambda \alpha \theta_0 - \theta_0)$
$\Delta \theta_5$	$= \lambda^4(1-\alpha)^4(\lambda \theta_0 + \alpha - \lambda \alpha \theta_0 - \theta_0)$
$\Delta \theta_N$	$= \lambda^{(N-1)}(1-\alpha)^{(N-1)}(\lambda \theta_0 + \alpha - \lambda \alpha \theta_0 - \theta_0)$

From this, the change in fractional coverage for any cycle is given by Eq. (6), where t_c is the time the element is exposed to the environment between exiting the contact and reentry.

$$\theta_{n,in} = 1 - (1 - \theta_{n-1,out})e^{(-\nu P t_c)} \quad (6)$$

Thus, the adsorption fraction is given by Eq. (7).

$$\alpha = 1 - e^{(-\nu P t_c)} \quad (7)$$

Substituting this expression for α into Eq. (3) and simplifying gives Eq. (8), which is a cycle-dependent solution for the entering fractional coverage.

$$\theta_{in} = \theta_0 (\lambda^n (e^{-\nu P t_c}) + (1 - e^{-\nu P t_c}) \left(\frac{1 - \lambda^n (e^{-\nu P t_c})}{1 - \lambda (e^{-\nu P t_c})} \right)) \quad (8)$$

The exposure time for one cycle (t_c) can be expressed as a track length (L) divided by the sliding speed (V), $t_c = L/V$, and the number of cycles can be expressed as the product of the sliding speed (V) and the cumulative run time (T) divided by the track length (L), $n = VT/L$. The fractional coverage of the surface entering the contact as a function of run time is given by Eq. (9).

$$\theta_{in} = \theta_0 (\lambda^{(VT/L)} (e^{-(VT/L)(\nu PL/V)}) + (1 - e^{-(\nu PL/V)}) \times \left(\frac{1 - \lambda^{(VT/L)} (e^{-(VT/L)(\nu PL/V)})}{1 - \lambda (e^{-(\nu PL/V)})} \right)) \quad (9)$$

The relationship between the entering fractional coverage (θ_{in}) and the average fractional coverage ($\bar{\theta}$) under the pin can be derived from the fractional removal equations developed by Blanchet and Sawyer [18], as shown in Eq. (10).

$$\bar{\theta} = \theta_{in} \frac{(1-\lambda)}{-\ln(\lambda)} \quad (10)$$

The average fractional coverage under the pin contact at any cumulative run time is found by substituting Eq. (9) into Eq. (10), which is done in Eq. (11).

$$\bar{\theta} = \frac{(1-\lambda)}{-\ln(\lambda)} \left(\theta_0 \lambda^{(VT/L)} e^{-(VT/L)(\nu PL/V)} + (1 - e^{-(\nu PL/V)}) \times \left(\frac{1 - \lambda^{(VT/L)} (e^{-(VT/L)(\nu PL/V)})}{1 - \lambda (e^{-(\nu PL/V)})} \right) \right) \quad (11)$$

Two nondimensional groups can be defined: normalized time $T^* = VT/L$, and normalized deposition $D^* = \nu PL/V$. Substituting these two nondimensional groups into Eq. (11) gives a dimensionless form of average fractional coverage under the contact in Eq. (12).

$$\bar{\theta} = \theta_0 \left(\frac{(1-\lambda)}{-\ln(\lambda)} \right) (\lambda^{T^*} (e^{-T^* D^*}) + \left(\frac{(1-\lambda)}{-\ln(\lambda)} \right) (1 - e^{-D^*}) \times \left(\frac{1 - \lambda^{T^*} (e^{-T^* D^*})}{1 - \lambda (e^{-D^*})} \right)) \quad (12)$$

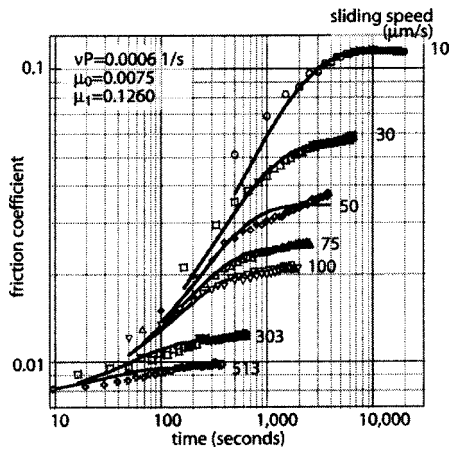


Fig. 1 Heimberg et al. experimental friction data and best fit as a function of time. The model fit obtained by holding the product $\nu P=0.00059 \text{ s}^{-1}$ constant but allowing the removal fraction to vary as a function of sliding speed.

Using a linear rule-of-mixtures the friction coefficient μ can be estimated by Eq. (13), where μ_0 is the friction coefficient of the nascent surface, and μ_1 is the friction coefficient of the surface with the adsorbed contaminants.

$$\mu = \mu_0 + \bar{\theta}(\mu_1 - \mu_0) \quad (13)$$

Results and Discussion

Heimberg et al. investigated the superlow friction behavior of a DLC coating in reciprocating sliding contact at speeds from 0.01 to 5 mm/s in dry nitrogen with a constant normal load [7]. The experimental details are described thoroughly in their publication and are briefly summarized here.

The time-dependent data were collected over a series of experiments that varied the sliding speed systematically from high to low or the exposure time from short to long. At sliding speeds of 1–5 mm/s, this coating had a friction coefficient of $\mu=0.007$, which is assumed to correspond to the friction coefficient of the nearly clean or nascent surface μ_0 . At sliding speeds of 10 $\mu\text{m/s}$, this coating had a friction coefficient near $\mu=0.12$, which was assumed to correspond to the friction coefficient of a nearly saturated or covered surface μ_1 . The wear track length for this experiment was 5 mm, and the normal load was 9.8 N. The coating was applied to both the hemispherically tipped pins, which were either 6.35 mm diameter sapphire or 12.7 mm diameter steel, and the counterface, which was H13 steel. The test environment was dry nitrogen that had a relative humidity and oxygen concentration of less than 1 percent. The published friction data from these tests was the average friction coefficient on each pass, which is assumed to be a reasonable approximation for the midpoint that was modeled here.

This model contains four parameters that were allowed to vary during the optimization routine that was employed. These parameters are a deposition term νP , a removal ratio λ , and friction coefficients for the nascent and covered surfaces, μ_0 and μ_1 respectively. It was assumed that νP , μ_0 , and μ_1 are constant for each data set. The removal ratio λ was allowed to vary as a function of speed.

The fit of Eq. (11) to the collected data (Fig. 1) gives a deposition term $\nu P=0.00059 \text{ s}^{-1}$, a nascent surface friction coefficient $\mu_0=0.0075$, and a covered surface friction coefficient $\mu_1=0.126$. The fraction removed, $1-\lambda$, systematically increases with increasing sliding speed (Fig. 2), which suggests that increasing power may increase removal efficiency.

Heimberg et al. also investigated the superlow friction behavior holding the sliding speed constant at 1 mm/s but varying the time

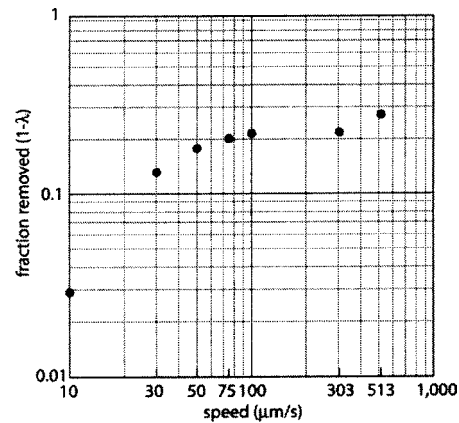


Fig. 2 Fraction of adsorbed species removed as a function of sliding speed. Derived from the model fit shown in Fig. 1.

between successive passes of the pin between 5 s and 162 s using the previously described protocol [7]. The fit of Eq. (11) to this collected data (Fig. 3) gives a deposition term $\nu P=0.00067 \text{ s}^{-1}$, a nascent surface friction coefficient $\mu_0=0.0057$, and a covered surface friction coefficient $\mu_1=0.136$. Surprisingly, the removal fraction, $1-\lambda$, systematically increased with decreasing dwell times (Fig. 4).

The fit of this model to the experimental data is excellent; however, it does raise some interesting questions. Namely, why would the removal fraction change with sliding speed and dwell time? There is no suitable hypothesis for increasing removal fraction with increasing sliding speed and decreasing dwell times. Although, in both cases the removal fraction is increasing with decreasing exposure time, which suggests that the exposure time dependence of the removal fraction may be compensating for something missing in the deposition model.

A couple of hypotheses can be offered. One hypothesis is that desorption of the contaminant species is occurring under the pin contact. As derived by Langmuir [17], the desorption rate increases monotonically with increasing surface temperature, and to the first order the dependence is to the square root of temperature. The low Peclet number suggests that stationary heat transfer analysis is appropriate, and, therefore, the temperature rise under the contact at any contaminated sites will be proportional to the sliding speed to the first power. However, fits to the constant speed tests showed systematic variations that do not support this

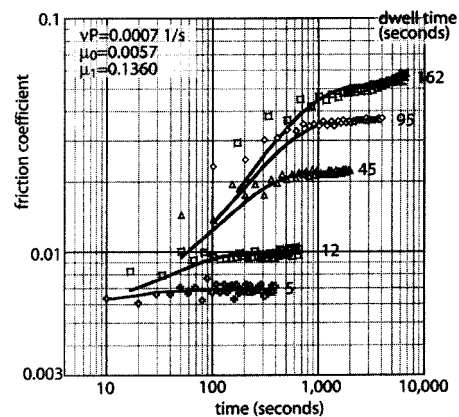


Fig. 3 Heimberg et al. experimental friction data and best fit as a function of time. The model fit obtained by holding the product $\nu P=0.00067 \text{ s}^{-1}$ constant but allowing the removal fraction to vary as a function of dwell time.

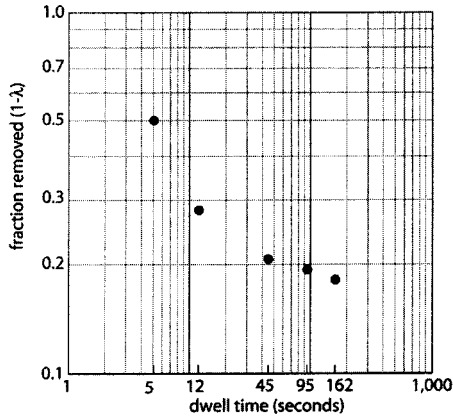


Fig. 4 Fraction of adsorbed species removed as a function of dwell time. Derived from the model fit shown in Fig. 3.

hypothesis. Another hypothesis is that the surface topography is changing during these experiments and this change is altering the removal rate. In both data sets the later experiments were less efficient at removing the contaminants than the earlier ones. This change in surface topography might also be enhancing the deposition rates, however, fits holding the removal ratio constant and allowing the deposition terms to vary did not fit the data well. Finally, since the later tests were also higher friction it may be that the removal fraction has a dependence on friction coefficient.

The parameters that were fit all gave remarkably reasonable results. The friction coefficients μ_0 and μ_1 were close to what were predicted prior to fitting and were similar for the two tests. The removal fraction, $1-\lambda$, varied from nearly zero to 50 percent, which is also quite reasonable. It is somewhat curious that the time constant for the adsorption rate found by fitting Eq. (11) to the data is between 1600 and 1800 s. This seems high for an adsorption process although dry nitrogen can have very little water and it may not be an adsorption process causing the increase in friction; rather, some other gas surface interaction [19].

Conclusions

The following conclusions were reached from this work:

1. A closed-form equation has been derived for the time-dependent fractional coverage of a surface film that follows Langmuir's deposition model coupled with a differential removal of fractional films.
2. The model fits the time-dependent speed excursions data of Heimberg et al. [7] for superlow friction DLC with a constant deposition rate if the removal fraction increases with increasing speed and decreasing dwell.

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Appendix

The approach used and detailed in this paper to develop a closed-form analytical solution for the fractional coverage of an adsorbed surface film in tribological contact is followed here for two other common adsorption models, the Elovitch equation and Henry's law. The approach is identical to what was previously described, including use of the fractional removal term λ . The model development offered here is minimally described and written as compactly as possible.

Elovitch. The Elovitch equation is an empirical model for adsorption rate that has a unique dependence on the surface fractional coverage:

$$\frac{d\theta}{dt} = \nu \exp(-\alpha\theta)$$

This model has no saturation point, and fractional coverage is allowed to proceed past unity. The first few terms of the inlet fractional coverage (θ_{in} values), letting $\beta = \alpha\nu t$ and $\gamma = \exp(\alpha\lambda\theta_0)$, are:

$$\theta_1 = \left(\frac{1}{\alpha}\right) \ln(\beta + \gamma)$$

$$\theta_2 = \left(\frac{1}{\alpha}\right) \ln(\beta + (\beta + \gamma)^\lambda)$$

$$\theta_3 = \left(\frac{1}{\alpha}\right) \ln(\beta + (\beta + (\beta + \gamma)^\lambda)^\lambda)$$

This repetition inside the natural log term can be compactly described as:

$$U_n = \beta + (U_{n-1})^\lambda$$

$$U_{n+1} = \beta + (U_n)^\lambda$$

Unfortunately, there is no closed-form solution for this recursive relationship; however, the equation can be easily used computationally.

Henry's Law. Henry's law [19] says that the time change of fractional coverage is equal to an adsorption rate ν , and is not dependent on the fractional coverage on the surface and, like the Elovitch model, has no saturation point:

$$\frac{d\theta}{dt} = \nu$$

The first few terms for the fractional coverage are:

$$\theta_{0in} = \theta_0$$

$$\theta_{0out} = \lambda\theta_0$$

$$\theta_{1in} = \nu t_c + \lambda\theta_0$$

$$\theta_{1out} = \lambda(\nu t_c + \lambda\theta_0)$$

$$\theta_{2in} = \nu t_c + \theta_{1out}$$

$$\theta_{2out} = \lambda\theta_{2in}$$

This results in a difference pattern of:

$$\Delta\theta_N = \lambda^{(N-1)}(\nu t_c + \lambda\theta_0 - \theta_0)$$

The resulting series expression is:

$$\theta_n = \theta_0 + \sum_{N=1}^n \lambda^{(N-1)}(\nu t_c + \lambda\theta_0 - \theta_0)$$

The closed-form solution for coverage based on cycle number then becomes:

$$\theta_n = \theta_0 + \left[\frac{1-\lambda^n}{1-\lambda}\right](\nu t_c + \lambda\theta_0 - \theta_0)$$

Taking the number of cycles to infinity gives a steady-state solution:

$$\theta_{SS} = \frac{\nu t_c}{1-\lambda}$$

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