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

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Abstract

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 [1], which is combined with the removal rate from Blanchet and Sawyer [2]. 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 [3], when the fractional removal term was allowed to increase with increasing sliding speed.

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 [4-7]. Testing of DLC films as solid lubricant coatings has shown them to possess low coefficients of friction, spanning the range μ=0.001 to 0.6 [6-9], although the testing conditions and type of DLC film (i.e., hydrogenated vs. 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 [3,7], has been theorized to be dependent on the amount of contaminants adsorbed on the rubbing surface [3].

Some attempts have been made to model the frictional behavior of DLC and other carbon films in various environments [6,10,11]. A current hypothesis is that the variations in friction coefficient with sliding speed in a pin-on-disk contact are the result of a competitive rate process that involves both the adsorption of a contaminant species on the surface of the diamond-like carbon and the removal of these species under the contact of the pin. Much like vapor-phase lubrication [12-18], 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 [1] and Blanchet and others [2,12-18]. 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.

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 [1] and Blanchet and Sawyer [2] 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 - θ_{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 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 Eqn. 1.

$$\theta_{n,in} = \theta_0 + \left[\sum_{N=1}^{n} \lambda^{(N-1)}(1-\alpha)^{(N-1)} \right](\lambda\theta_0 + \alpha - \lambda\alpha\theta_0 - \theta_0) \qquad \text{Eqn 1}$$

Quite fortuitously this series has a closed-form expression, given in Eqn 2.

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

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

$$\theta_{in} = \theta_0 \left(\lambda(1-\alpha)\right)^n + \alpha\left(\frac{1-\lambda^n(1-\alpha)^n}{1-\lambda(1-\alpha)}\right)$$ Eqn 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 Eqn 4.

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

This expression agrees with steady-state expressions developed previously by Sawyer and Blanchet [12]. 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 (v), the gas pressure (P), and the nascent surface area fraction ($1-\theta$).

$$\frac{d\theta}{dt} = vP(1-\theta)$$ Eqn 5

From this, the change in fractional coverage for any cycle is given by Eqn 6, where t_c is the time the element is exposed to the environment between exiting the contact and re-entry.

$$\theta_{n,in} = 1 - (1-\theta_{n-1,out})e^{(-vPt_c)}$$ Eqn 6

Thus, the adsorption fraction is given by Eqn 7.

$$\alpha = 1 - e^{(-vPt_c)} \qquad\qquad \text{Eqn 7}$$

From the differential removal model proposed by Blanchet and Sawyer [2], the removal ratio (λ) is a function of the normal load on the pin (F) and an empirical removal variable (K') as given in Eqn 8.

$$\lambda = e^{(-K'F)} \qquad\qquad \text{Eqn 8}$$

Substituting these expressions for α and λ into Eqn. 3 and simplifying gives Eqn 9, which is a cycle-dependent solution for the entering fractional coverage.

$$\theta_{in} = \theta_0\, e^{\left(-n\left(K'F + vPt_c\right)\right)} + \left(1 - e^{(-vPt_c)}\right) \left[\frac{1 - e^{\left(-n\left(K'F + vPt_c\right)\right)}}{1 - e^{\left(-\left(K'F + vPt_c\right)\right)}} \right] \qquad\qquad \text{Eqn 9}$$

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 Eqn 10.

$$\theta_{in} = \theta_0\, e^{\left(-\left(K'F+\frac{vPL}{V}\right)\frac{TV}{L}\right)} + \left(1-e^{\left(-\frac{vPL}{V}\right)}\right)\left[\frac{1-e^{\left(-\left(K'F+\frac{vPL}{V}\right)\frac{TV}{L}\right)}}{1-e^{\left(-\left(K'F+\frac{vPL}{V}\right)\right)}}\right] \qquad \text{Eqn 10}$$

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 [2], as shown in Eqn 11.

$$\bar{\theta} = \theta_{in}\frac{(1-\lambda)}{-\ln(\lambda)} = \theta_{in}\frac{\left(1-e^{(-K'F)}\right)}{K'F} \qquad \text{Eqn 11}$$

The average fractional coverage under the pin contact at any cumulative run time is found by substituting Eqn 10 into Eqn 11, which is done in Eqn 12.

$$\bar{\theta} = \theta_0\frac{\left(1-e^{(-K'F)}\right)e^{\left(-\left(K'F+\frac{vPL}{V}\right)\frac{TV}{L}\right)}}{K'F} + \frac{\left(1-e^{\left(-\frac{vPL}{V}\right)}\right)\left(1-e^{(-K'F)}\right)}{K'F}\left[\frac{1-e^{\left(-\left(K'F+\frac{vPL}{V}\right)\frac{TV}{L}\right)}}{1-e^{\left(-\left(K'F+\frac{vPL}{V}\right)\right)}}\right] \qquad \text{Eqn 12}$$

Three nondimensional equations can be defined: normalized load $F* = K'F$, normalized time $T* = VT/L$, and normalized deposition $D* = vPL/V$. Substituting these three nondimensional equations into Eqn 12 gives a dimensionless form of average fractional coverage under the contact.

$$\bar{\theta} = \theta_0 \frac{\left(1-e^{(-F^*)}\right)e^{(-(F^*+D^*)T^*)}}{F^*} + \frac{\left(1-e^{(-D^*)}\right)\left(1-e^{(-F^*)}\right)}{F^*}\left[\frac{1-e^{(-(F^*+D^*)T^*)}}{1-e^{(-(F^*+D^*))}}\right] \qquad \text{Eqn 13}$$

Using a linear rule-of-mixture the friction coefficient μ can be estimated by Eqn 14, 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.

$$\mu = \mu_0 + \bar{\theta}\left(\mu_1 - \mu_0\right) \qquad \text{Eqn 14}$$

Results

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 [3]. 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. 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 nascent surface μ_0. At sliding speeds of 10 µm/s, this coating had a friction coefficient near $\mu = 0.12$, which was assumed to correspond to the friction coefficient of the saturated 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 partial pressure of less than 1%.

A best fit using Eqn 12 to the collected data (figure1) was found by holding the deposition terms νP constant at 0.000436 s^{-1} for all the sliding speeds and allowing the removal coefficient K' to vary at different sliding speeds. Plotting the removal percentage versus sliding speed (figure 2) shows that the percentage of film removed increases monotonically with increasing sliding speed.

Heimberg *et al.* also investigated the superlow friction behavior holding the sliding speed constant at 1 mm/s but varying the time between successive passes of the pin between 5 s and 165 s using the previously described protocol [3]. For these experiments the nascent surface friction coefficient μ_0 was reported as $\mu_0 = 0.004$. A best fit using Eqn 12 to the collected data (figure 3) was found by holding the deposition terms νP constant at 0.0003 s^{-1} but allowing the removal fraction to vary over a range of $\lambda \pm 0.108$, with an average value of $\lambda = 0.466$.

Discussion

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? 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 [1], the desorption rate increases monotonically with increasing surface temperature, and to the first order the dependence is to the square root of temperature. The friction coefficients are very low, as are the sliding speeds in this contact. Correspondingly, the low Peclet number suggests that stationary heat transfer analysis is appropriate. Therefore, the

temperature rise under the contact at any contaminated sites will be proportional to the sliding speed to the first power. It seems unlikely that these surfaces would have temperature rises much in excess of a few degrees Celsius, which is probably not high enough to greatly affect the desorption rate. Another hypothesis is that the surface topography is changing during these experiments in such a way that the later experiments (lower speed) are less efficient at removing the contaminants. Although the model was fit assuming the deposition parameters were not changing, changes in the surface topography may be affecting the deposition rate, and the equations could be fit by allowing both the deposition and removal terms to vary. Such fits do not look appreciably different from figure 1.

Another curiosity is that the time constant for the adsorption rate found by fitting Eqn 12 to the data is over 2,000 seconds. This high value seems very unlikely for experiments that were run in dry nitrogen at atmospheric pressure and room temperature, and not ultrahigh vacuum. Following the hypothesis that adsorbed water vapor is responsible for the variations in friction coefficient, it seems unlikely that the partial pressure of water vapor in the dry nitrogen could be this low.

When fitting the data of varying hold times while maintaining the sliding speed constant at 1 mm/s, the average removal fraction was $\lambda = 0.466$. This value is in keeping with the observation (figure 2) that the removal efficiency increases with increasing sliding speed. Also noteworthy is that the time constant for the deposition rate is very similar to the time constant found previously in fitting the data collected during variations in sliding speed. The variations in removal fraction of $\lambda \pm 0.108$ cannot be explained.

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.* [3] for superlow friction DLC with a constant deposition rate if the removal fraction increases with increasing speed.

3) The model fits the time-dependent hold time data of Heimberg *et al.* [3] for super-low friction DLC with a constant deposition rate and variations in removal fractions of ~23%.

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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:

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

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 $\beta = \alpha v t$

and $\gamma = \exp(\alpha\lambda\theta_0)$, are:

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

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

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

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 v, and is not dependent on the fractional coverage on the surface and, like the Elovitch model, has no saturation point:

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

The first few terms for the fractional coverage are:

$$\theta_{0in} = \theta_0$$
$$\theta_{0out} = \lambda\theta_0$$
$$\theta_{1in} = vt_c + \lambda\theta_0$$
$$\theta_{1out} = \lambda(vt_c + \lambda\theta_0)$$
$$\theta_{2in} = vt_c + \theta_{1out}$$
$$\theta_{2out} = \lambda\theta_{2in}$$

This results in a difference pattern of:

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

The resulting series expression is:

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

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

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

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

$$\theta_{SS} = \frac{vt_c}{1-\lambda}$$

Figure Captions

Figure 1: Heimberg *et al*. experimental friction data and best fit as a function of time. The model fit obtained by holding the product $\nu P = 0.000436$ s^{-1} constant but allowing the removal fraction to vary as a function of sliding speed.

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

Figure 3: Heimberg *et al*. experimental friction data and best fit as a function of time. The model fit obtained by holding the product $\nu P = 0.0003$ s^{-1} constant but allowing the removal fraction to vary over a range of $\lambda \pm 0.108$ with an average value of $\lambda = 0.466$.

Table Captions

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

Table 2: Analytical expressions for the difference between the entering fractional coverage for the first few cycles.
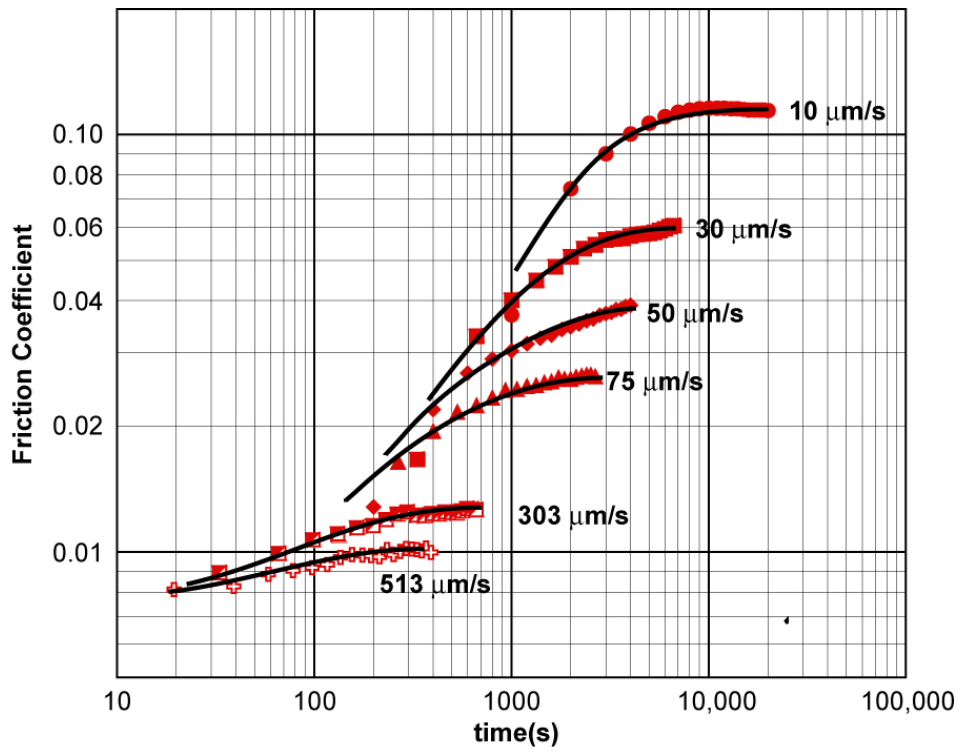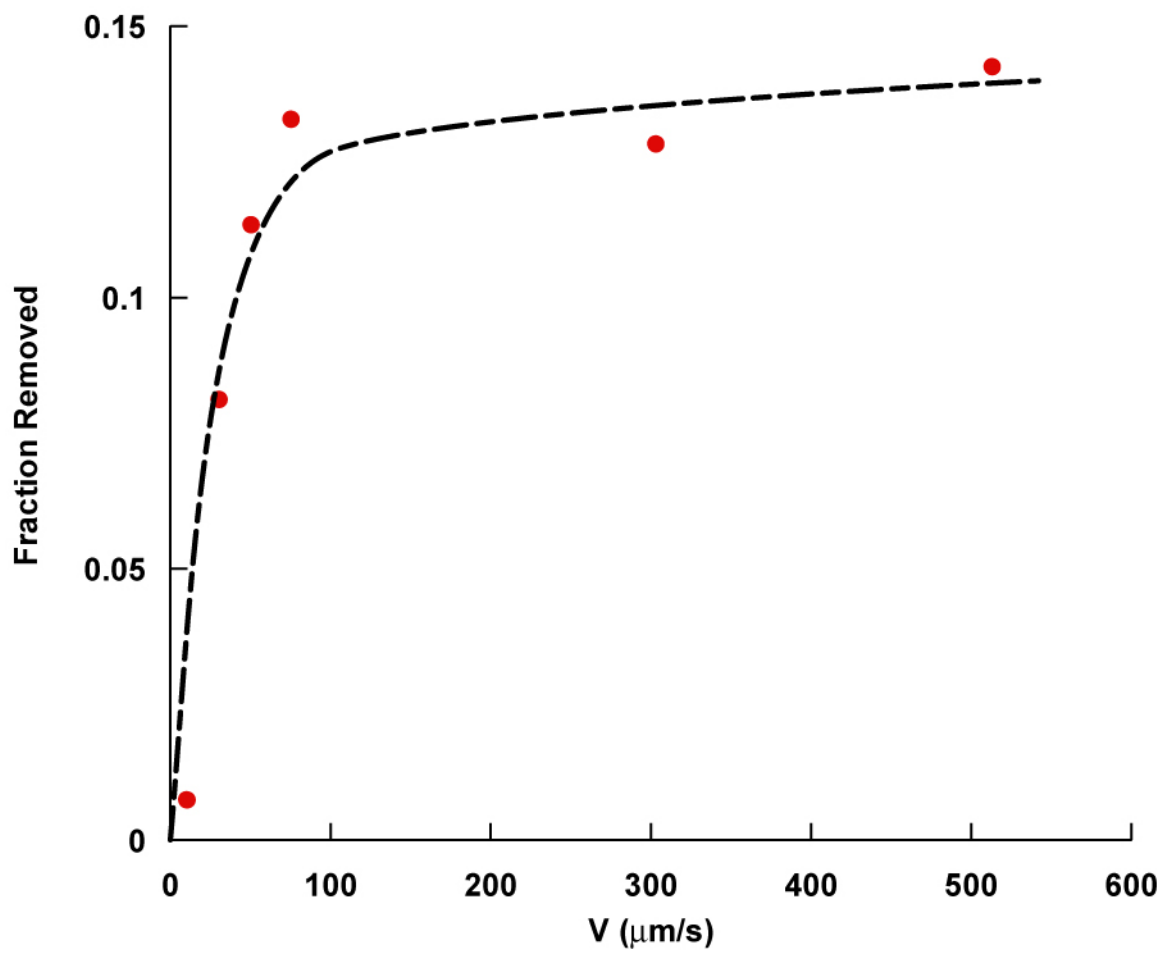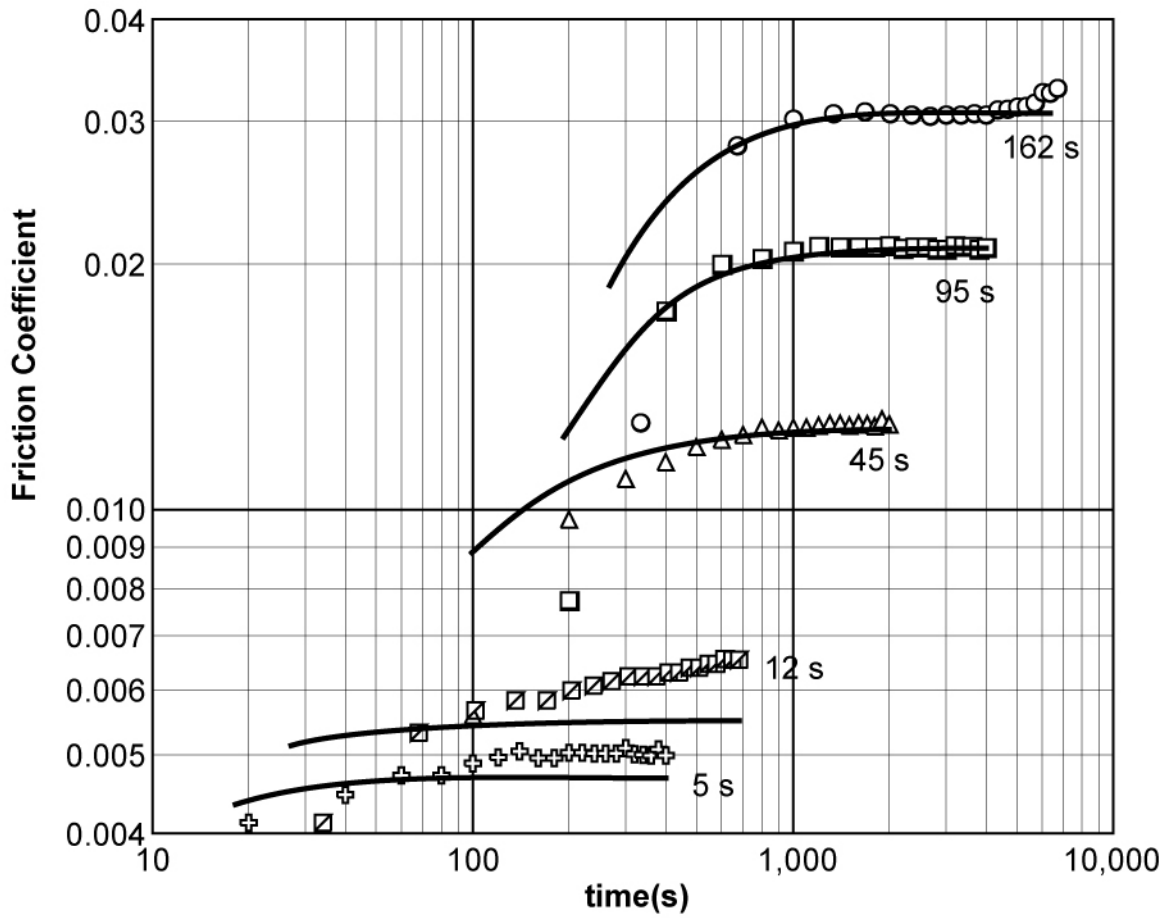
Figure 1

Figure 2

Figure 3

Table 1

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}	$= \lambda\theta_{2in}$	$= \lambda\left(\lambda^2\theta_0 + \lambda\alpha - 2\lambda^2\alpha\theta_0 + \alpha - \lambda\alpha^2 + \lambda^2\alpha^2\theta_0\right)$
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}	$= \lambda\theta_{3in}$	$= \lambda\left(\lambda^3\theta_0 + \lambda^2\alpha - 3\lambda^3\alpha\theta_0 + \lambda\alpha - 2\lambda^2\alpha^2 + 3\lambda^3\alpha^2\theta_0 + \alpha - \lambda\alpha^2 + \lambda^2\alpha^3 - \lambda^3\alpha^3\theta_0\right)$

Table 2

$$\Delta\theta_1 = \lambda\theta_0 + \alpha - \lambda\alpha\theta_0 - \theta_0$$

$$\Delta\theta_2 = \lambda(1-\alpha)(\lambda\theta_0 + \alpha - \lambda\alpha\theta_0 - \theta_0)$$

$$\Delta\theta_3 = \lambda^2(1-\alpha)^2(\lambda\theta_0 + \alpha - \lambda\alpha\theta_0 - \theta_0)$$

$$\Delta\theta_4 = \lambda^3(1-\alpha)^3(\lambda\theta_0 + \alpha - \lambda\alpha\theta_0 - \theta_0)$$

$$\Delta\theta_5 = \lambda^4(1-\alpha)^4(\lambda\theta_0 + \alpha - \lambda\alpha\theta_0 - \theta_0)$$

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