

Modeling the Tribochemical Aspects of Friction and Gradual Wear of DLC Films

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Background: Diamond-Like Carbon (DLC) Films

- [Amorphous carbon](#) (a-C) films used as protective coatings in computer hard disks
- sp^2 [trigonal] and sp^3 [tetrahedral] hybridizations of carbon randomly present (some sp^1 [linear] present).
- [Amorphous hydrogenated carbon](#) (a-C:H) films contain hydrogen.
- Characteristics commonly used are
 - sp^3/sp^2 ratio
 - Film density
 - [Hydrogen](#) concentration

Diamond-Like Carbon (DLC) Film Properties

- If the film density and sp^3/sp^2 ratio are high and the hydrogen concentration low (up to 30%) then films are considered hydrogenated diamond-like carbon (DLC:H) films.
- DLC:H films are associated with high wear resistance and hardness, which is caused by the different hydrogen concentrations.

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Background: Friction – Historical View

- **Leonardo da Vinci** (according to Kragelsky and Shchedrov)
- **Amontons' Law** – 1699 (verified by Kotelnikov – 1774)
$$\mu = F_f / p$$
- **Coulomb** – 1821 (introduced constant term associated with sticking of surfaces)
$$F_f = A + \mu p$$
- **Tomlinson** – 1929 (friction due to lattice oscillations of mating surfaces)
- **Derjaguin** – 1934 (distinguishing between true friction coefficient μ_t and the apparent friction coefficient μ_a)

$$F_f = \mu_t (Sp_0 + P) = \mu_a P,$$

(where $\mu_t Sp_0$ represents the tangential components of the molecular forces.)

- **Zhuravlev** – 1940 (statistical model of multiple contacts similar to Greenwood-Williamson – 1966)

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Friction Modeling

Various explanations for the friction phenomena,
primarily [molecular adhesion](#) and [mechanical interaction](#):

$$F_f = F_{f,mol} + F_{f,mech}$$

The measured friction coefficient can be represented as:

$$\mu = \mu_{mech} + \mu_{mol,1} + \mu_{mol,2} \quad (\text{see pictures next slide})$$

μ_{mech} : Mechanical effect, in particular by interlocking protuberances of the roughness

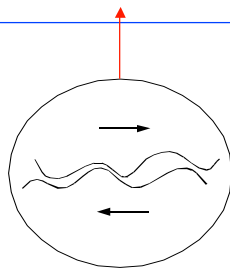
$\mu_{mol,1}$: Breaking of interatomic bonds between the adsorbate and a surface

$\mu_{mol,2}$: All other molecular effects, in particular by the lattice oscillation mechanism

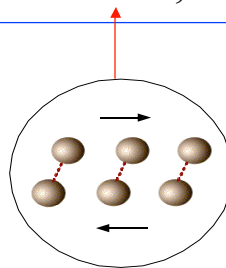
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Schematic Diagrams of Each Term

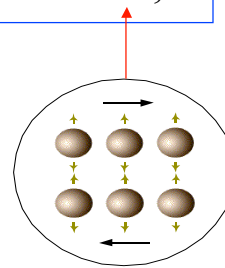
$$\mu = \mu_{mech} + \mu_{mol,1} + \mu_{mol,2}$$



Mechanical interactions



Breaking of interatomic bonds



Lattice oscillations
Thermal vibrations
Other molecular effects

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DLC Film Friction

- **DLC** friction coefficient range from 0.001 – 0.6
- Mainly due to differences in the sp^3/sp^2 ratio and **hydrogen** concentration. (Erdemir, 2001)
- **Hydrogen** may passivate surface which prevents more active adsorbates from adsorbing to surface.

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DLC Film Application



- Protective overcoats
- Typically very thin (order of nanometers), for application on magnetic disks and read-write heads.
- Films have high wear resistance due to the low friction coefficients and possibly the high hardness.
- Electron field-emission applications

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Modeling of Friction

- Friction behavior can strongly depend on the presence of water vapor and [oxygen](#).
- Addition of oxygen seen to:
 - Reduce friction of [graphite](#) (Zaidi et al., 1990)
 - Reduce friction of [DLC](#) (Erdemir, 2001)
 - Increase friction of [DLC:H](#) (Erdemir, 2001)
- DLC:H is typically passivated by hydrogen atoms, though when [hydrogen](#) is removed gaseous species may adsorb to the active surface sites ([adsorption](#)).
- Adsorbed species interact with the counterface, where during sliding the atomic bond between adsorbate and counterface may be broken ([desorption](#)). Adsorbed species are more likely to interact because they are chemically active, unlike the adsorbed [hydrogen](#).

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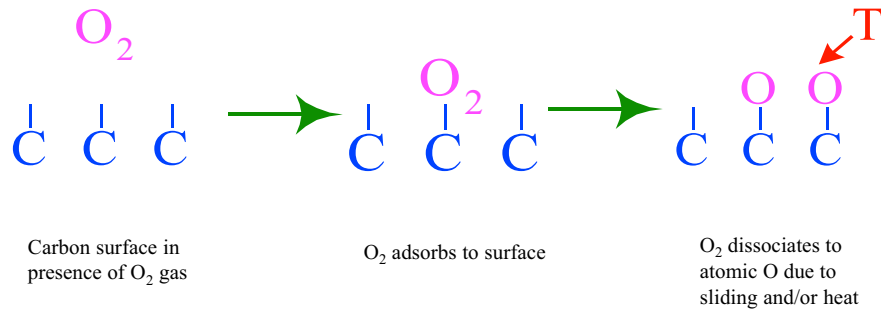
Modeling of Friction due to Adsorbates

Two primary areas of focus:

1. [Adsorption Modeling](#) – By using the Elovich equation, coverage of active surface sites is modeled based on the sliding velocity.
2. [Desorption Modeling](#) – Breaking of atomic surface bonds modeled using a probability of adsorbate removal.

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Adsorption Modeling



If **hydrogen** is present on the surface then there will be an associated probability, p , for hydrogen removal due to mechanical action, which will allow adsorption of gaseous species to the surface.

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Adsorption Modeling

When studying adsorption, it is necessary to represent the surface by the amount covered by adsorbed species, the coverage θ :

$$\theta = \frac{N_c}{N}$$

Where N_c is the number of surface sites occupied by adsorbate, N is the total number of surface sites.

Adsorption kinetics can be described by the Elovich equation:

$$\frac{d\theta}{dt} = B e^{-\alpha\theta}$$

After integration:

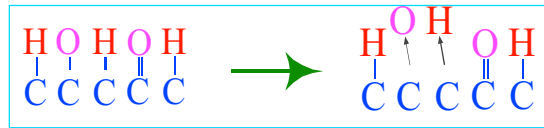
$$\theta(t) = \frac{1}{\alpha} \ln \left[e^{\alpha\theta_0} + B\alpha(t - t_0) \right]$$

Which gives the coverage at any time instant t .

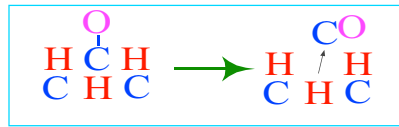
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Desorption Modeling

- Adsorbate is assumed to be removed by mechanical breaking of bonds due to sliding.
- Bonds may be that of C-O, C=O, or C-H. For example:



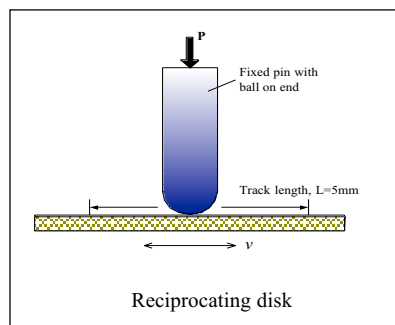
- Also, DLC:H films may wear by CO or CO₂ desorbing from surface due to the weak C-H bonds in the film structure.



- Ab initio calculations using Gaussian98 show that the bond strengths for C-H (295kJ/mol) were lower than for C-C (523kJ/mol) or C-O (1447kJ/mol).
- A probability of adsorbate removal is used in the desorption modeling.

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Modeling Friction based on a reciprocating ball-on-disk experiment (Heimberg, et al., 2001)



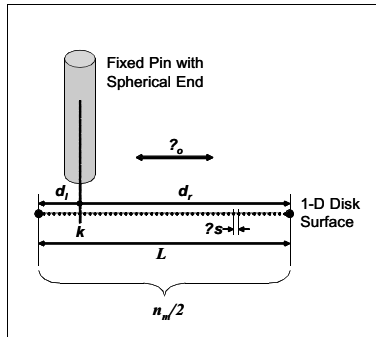
Both contacting surfaces coated with 1mm thick DLC:H films.

$$\mu = \frac{F}{P}$$

- Disk sliding beneath pin creates a lateral friction force, F , measured by a load cell.
- Velocity, v , was varied between 10 - 513 μ m/s.

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Model of Surface Adsorbate Coverage of Reciprocating Disk



Adsorbate coverage depends on $\tau(k, i)$, the time between passes at a specific point,

$$\text{For } L \rightarrow R: \tau(k, i) = d_l/v(i-1) + d_l/v(i)$$

$$\text{For } R \rightarrow L: \tau(k, i) = 2d_r/v(i)$$

(k = position; i = cycle number)

Using the Elovich equation:

$$\theta(k, i) \Big|_{t+\Delta t(k, i)+0^+} = \ln \left[\exp \left(a \left(\theta(k, i) \Big|_{t+0^-} + [\theta(k, i)] \right) + \alpha B \Delta t(k, i) \right) \right] \alpha$$

Where $t + 0^-$ is the time just before k -th point and $t + \tau(k, i) + 0^+$ is the time just after the k -th point.

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Coverage Model Continued

The jump in coverage (desorption), $[\theta(k, i)]$, is proportional to $\theta(k, i) \Big|_{t+0^-}$ thus:

$$[\theta(k, i)] = p \theta(k, i)$$

where p is the probability of breaking a surface bond and its value is related to the surface roughness of the sample. p is assumed constant, but may vary from sample to sample.

Using the desorption term, the coverage can be written:

$$\theta(k, i) \Big|_{t+\Delta t(k, i)+0^+} = \ln \left[\exp \left(a \theta(k, i) \Big|_{t+0^-} (1 - p) + \alpha B \Delta t(k, i) \right) \right] \alpha$$

which includes the adsorption and desorption kinetics.

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Model Constants

μ_c – Baseline friction coefficient, based on high-speed (1053 $\mu\text{m/s}$) sliding velocity.

α – Adsorption coefficient.

B – First-order constant in Elovich equation (order of 10^{-4}s^{-1}).

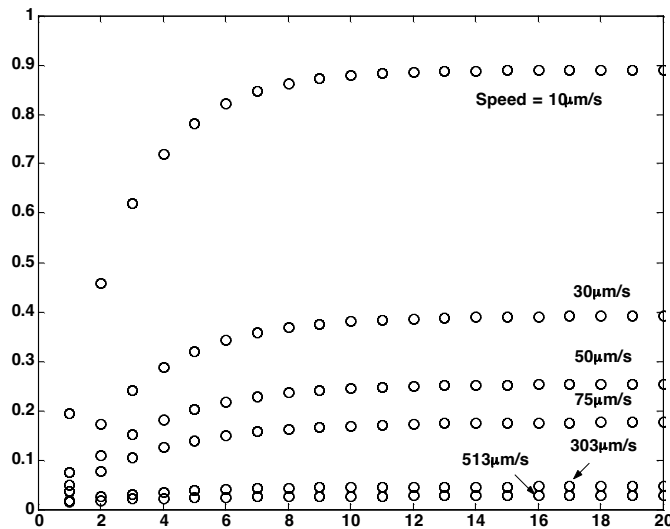
p – Adsorbate removal probability – related to the surface roughness.

$\theta(0)$ – Initial coverage.

Many of the constants found from curve fitting to experimental data, though model results compare well to entire set of experimental data \rightarrow Physics Correct

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Model Results – Surface Coverage



$\alpha = 0.6$
 $B = 4.1 \times 10^{-4} \text{ s}^{-1}$
 $p = 0.14$
 $\theta(0) = 0.001$

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Model of Friction based on surface coverage

$$\mu = \mu_c + \mu_{mol,1}$$

where $\mu_c = \mu_{mech} + \mu_{mol,2} = \text{const.}$

The molecular friction, $\mu_{mol,1}$, is proportional to the number of interacting bonds that are mechanically broken, i.e., $[\theta(k,i)]^p$

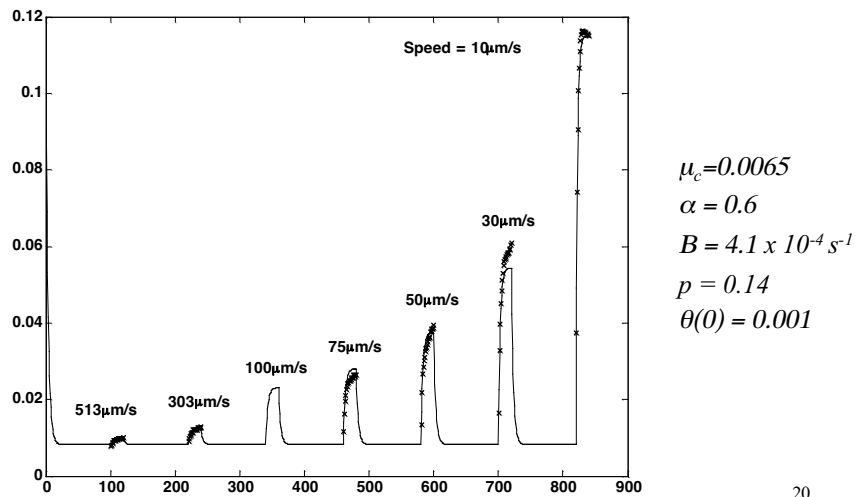
The average friction coefficient for the i -th cycle is given as,

$$\mu(i) = \mu_c + \frac{1}{n_m} \sum_{k=1}^{n_m} \mu_{mol,1}(i,k) = \mu_c + \frac{c}{n_m} \sum_{k=1}^{n_m} [\theta(k,i)]^p$$

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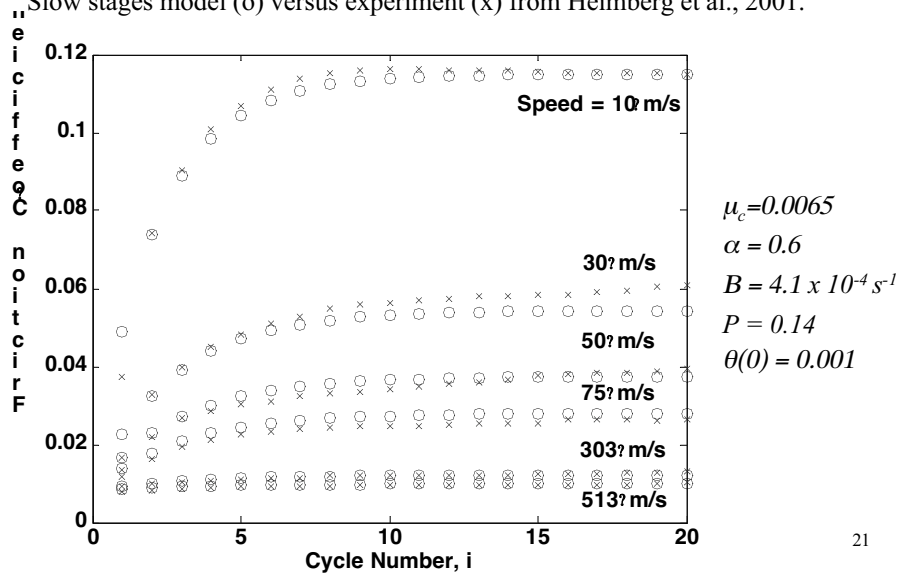
Results – DLC Friction

Entire speed range model (line) versus experimental results (x's) from Heimberg et al., 2001.



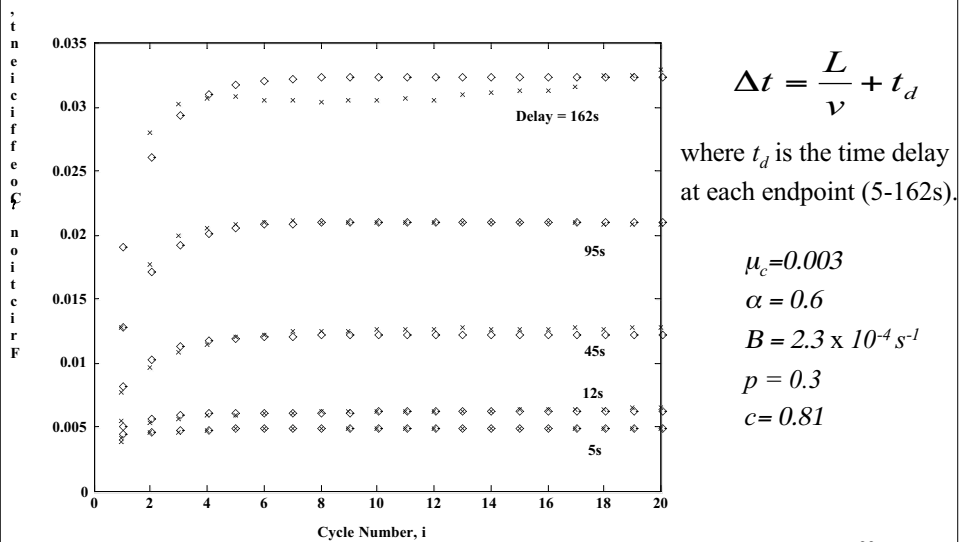
Results – Friction

Slow stages model (o) versus experiment (x) from Heimberg et al., 2001.



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Results – Friction of Time-Delayed Experiments



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Conclusions

- Friction coefficient can be represented as a summation of terms based on the mechanical interlocking of surfaces, lattice and thermal vibrations, and the breaking of interatomic bonds.
- The interatomic molecular friction is related to the coverage of adsorbates on the surface and is modeled by using adsorption and desorption kinetics.
- Results of the friction model based on coverage compares well with published experimental friction results for DLC:H films in a ball-on-disk setup.
- Bond energies from *ab initio* calculations showed that a likely model of DLC:H film wear is by CO and CO₂ desorption from the surface.

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