# Toward a Stochastic Theory of Wetting

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## Summary

Both microscopic and macroscopic forces influence dynamic wetting. However, there is a regime of wetting governed by molecular kinetics. Standard interpretation of Arrhenius dependence involves an activation energy representing the energy difference between the reactant and transition states. The standard kinetic model of wetting invokes contact line friction exhibiting an activation energy that scales with the work of adhesion. But molecular dynamics show mass transfer between effectively parallel liquid and solid interfaces. This work addresses the question: how can an activation energy for adsorption depend on the energy of the adsorbed (product) state rather than the liquid (reactant) state? The simplest explanation is a variation on the Kramers diffusion theory of chemical reactions that allows for variation in dynamical friction as molecules cross the gap. These effects may be present in other activated processes in condensed phases.

## Background

The motion of a liquid – gas interface moving across a solid surface is a complex process influenced by forces that range from molecular to macroscopic scales[1]. However, in the limit of low capillary number the oldest theory of dynamic wetting, the molecular kinetic theory[2,3] (MKT) is useful in correlating the speed and apparent contact angle of dynamic wetting. The MKT describes dynamic wetting as being the result of molecular level displacements that –in the limits of either low liquid surface tension, high density of solid liquid interaction sites per unit area, or small deviations from the equilibrium contact angle—proceed at a speed $U$ given by

$$U = \frac{\gamma_L}{\zeta}(\cos(\theta^0) - \cos(\theta_d))$$

Here $\zeta$ is referred to as the contact line friction (per unit length of contact line) and $\gamma_L$ is the surface energy of the coating liquid. The current form of the MKT[4] gives a correlation for the contact line friction

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$$\zeta = \frac{\eta_L v_L}{\lambda^3} e^{\left(\frac{\varphi W_a}{n k_B T}\right)}$$

Here $\eta_L$ is the liquid viscosity, $v_L$ is the unit flow volume (nominally the molecular volume), $W_a$ is the work of adhesion, $n$ is the number of sites for liquid adsorption per unit area, and $k_B$ is Boltzmann's constant. Ideally, φ is one; however, the data for different systems are scattered within the range $0.25 \leq \varphi \leq 1.0$. One of the great successes of the MKT is its ability to relate a molecular mechanism with macroscopic observables such as dynamic contact angle and the work of adhesion. However, there is no clear consensus on the exact nature of the contact line friction at this writing.

While the image associated with the MKT is of a liquid phase attached to a solid at a distinct contact line (at least in an ensemble average sense), there is an extensive literature[1] ranging from continuum descriptions to molecular dynamics along with experimental evidence documenting a region of slip that occurs at the apparent contact line. Thompson and Troian[5] provide a molecular mechanism for momentum transfer in the slip region: molecules of liquid that approach the surface become entrained by the corrugations in the surface potential.

At an intuitive level, the idea of surface corrugations providing a frictional force that scales with the work of adhesion seems reasonable. However, from a standpoint of chemical kinetics it presents some significance challenges. First, the standard kinetic theories focus on the reactant well not the product well. The goal of this work is to seek –in the spirit of Ockham's razor-- the simplest kinetic model that can reconcile the Thompson and Troian mechanism (an adsorption process) with the dependence of contact line friction on the work of adhesion (a property of the product state).

H. A. Kramers[6] gave three theories for predicting rate constants valid in the limits of low, moderate to high, and high degrees of dynamical friction for two potentials. Dynamical friction is defined phenomenologically by the Langevin equation[7]; however, the term is often avoided using Einstein's formula for the Brownian diffusion of spherical particles or, following Langevin's original exposition, related to the viscosity through the Stokes Einstein relationship. Chanrdasekhar[8] established the physical basis for variations in the dynamical friction coefficient (albeit for sparsely populated gravitational systems that have mean free paths on the order of the size of the system).

## Current work

A molecule passing through a gap between liquid and solid interfaces is subject to complex forces. Polarizability (dispersion) forces will attract the molecule to both interfaces. Making the common assumption of pairwise additivity, the leading behavior of this attraction is a potential energy that varies as the sum of the attraction to each interface. As the molecule nears an interface, short term repulsions that prevent the molecule from penetrating the solid surface and limit the binding energy to the liquid interface become important. However, the assumption of equilibrium in the reactant well renders the exact nature of the repulsive term immaterial – provided the well depth and curvature are known. Figure 1 compares two common approximations to the attractive potential with a somewhat arbitrary algebraic repulsive term that can be used to fit well depth and curvature.

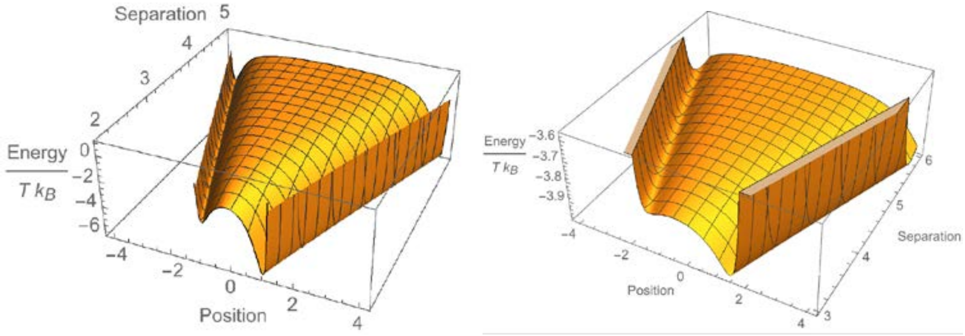

Figure 1 – Two common potential functions as function of separation. The 3-9 Mie potential (on the left) represents the leading behavior of the full Hamaker attraction shown on the right (paired with the same $z^{-9}$ repulsive potential). The Hamaker constant is matched to give similar "reactant" well depth to the Mie case; however, the longer range of the attraction in the Hamaker case reduces the depth of the "product" well.

At large separation, the potential surface is asymptotically flat near the center of the gap and the region between the two wells may become filled with air (in which case other complications arise). This is the regime considered by Larson and Lightfoot[9]. Although Lightfoot[10] modeled the effect of some analytically convenient variations in the friction near the surface for this case, those do not include friction varying across the barrier. At intermediate separation, the barrier is neither asymptotically flat nor well approximated by a parabola. All asymptotic results for this case generated to date are too algebraically complex to generate useful physical insight. At low separation, the range of the attractive terms causes a marked drop in the barrier between the wells (with a corresponding increase in the rate of crossing the gap). This is the most obvious way that the attraction to the solid surface affects the rate of molecules passing between the liquid and adsorbed states: the stronger the attraction to the solid surface, the lower the barrier, the higher the rate constant, and –within the context of the Thompson and Troian mechanism— the higher the rate of momentum transfer between the liquid and solid interfaces. However, at low separation, the barrier and the wells look to be reasonably approximated by the piecewise parabolic potential used by Kramers:

$$E(x) \approx E(a) + \frac{(2\pi\omega_a)^2}{2}(x-a)^2 \tag{1a}$$

near the bottom of the "reactant" well while near the barrier (centered at x=b)

$$E(x) \approx E(b) - \frac{(2\pi\omega_b)^2}{2}(x-b)^2. \tag{1b}$$

To talk about effects of the product state, this is augmented with a third disjoint domain (centered at x=c)

$$E(x) \approx E(c) + \frac{(2\pi\omega_c)^2}{2}(x-c)^2;\ for\ x \approx c \tag{1c}$$

In the limit of high dynamical friction Kramers modeled the escape problem using Smoluchowski's diffusion equation lumping the friction into a constant K and a viscosity. Chandrasekhar[11] gives a clearer definition of the dynamical friction and the more proper form of the equation is

$$\frac{\partial\rho}{\partial\tau} = \frac{\partial}{\partial\xi}\left[\frac{k_B T}{m\beta}\left(\frac{\partial\rho}{\partial\xi} + \frac{\rho}{k_B T}\frac{dE}{d\xi}\right)\right]$$

In this case, the reaction coordinate $\xi$ is merely the distance across the gap. Defining

$$\begin{gathered} \xi = x \\ \tau = \beta t \\ E = k_B T V \\ w = \rho\sigma \end{gathered}$$

gives the dimensionless form of the Smoluchowski equation:

$$\frac{\partial w}{\partial t} = \frac{\partial}{\partial x}\left[\frac{1}{h(x)}\left(\frac{\partial w}{\partial x} + \frac{dV}{dx}w\right)\right]$$

Here $\sigma$ is a characteristic dimension of the molecules (e.g., the collision radius), w is the number density per unit x and

$$h(x) = \frac{\beta(x)}{\beta_0}$$

For present purposes $\beta_0$ is taken as the friction exhibited at the liquid surface (i.e., near $x$=$a$).

The dimensionless Kramers Pontryagin formula for the rate constant for escape over a barrier in the presence of variable friction is generalized to

$$k = \frac{1}{\int_a^c he^V\,dx \int_{Reactant\ well} e^{-V}dx} \tag{2}$$

Given the disjoint nature of the piecewise parabolic potential, the only tractable limit is if the barrier (1b) is high enough that the extension of the range of integration of each term in this equation can be confined to one subdomain that is then approximated by an infinite range with reasonable accuracy (as assumed by Kramers).

The simplest case of interest is assuming the dynamical friction coefficient is constant in each subdomain. For this case, the dimensionless one-way rate constant is:

$$k = \frac{2\pi\omega_a\omega_b e^{V_a - V_b}}{h_b}$$

This result seems trivially different from the Kramers formula (merely requiring the dynamical friction coefficient to be evaluated at the maximum of $e^{V(x)}$). However, this simple result provides the key to understanding the effect of variable friction on the rate of wetting or, in the general sense, on the rate of passage of "particles" over a barrier.

Dynamical friction is defined by the Langevin equation.

$$\frac{du}{dt} = -\beta u + \bar{F}(x)/m + L(t)$$

*L(t)* is the fluctuating Langevin acceleration term while $\bar{F}$ is the mean force on the particle. In the absence of the fluctuating force, the particle would eventually decay to a motionless state. The fluctuating force creates a dynamic balance that keep the particle in motion with an average kinetic of $k_BT/2$ per degree of freedom (satisfying the equipartition theorem). The dynamical friction coefficient is directly proportional to the ensemble average $<L(t)L(t')>$ (e.g., in the textbook theory $<L(t)L(t')> = 2\beta k_B T\delta(t-t')$).

While the net kinetic energy generated by the fluctuations is fixed; fluctuations must come from identified physical mechanisms[12]. Fluctuating accelerations can come from collisions with other particles; however, in the present case, the long range of attractive forces with respect to the repulsive forces suggests that fluctuations in the attraction of molecules to the two surfaces would be expected to dominate the fluctuating forces. Figure 1 shows the mean field a particle would feel between two idealized surfaces based on dispersion forces; however, reducing the three-dimensional force on a particle to a one-dimensional field requires assumptions on the homogeneity of the surfaces and integration over the two in-plane physical dimensions. The actual field between the two surfaces at any physical point and instant in time may look quite different from Figure 1 depending on thermal vibration of the molecules that comprise the interfaces, the alignment of any molecular structure at the liquid surface with corrugations in the surface potential, the motion of the corrugations relative to the liquid, and asperities on the surface. Having already assumed pairwise additivity of forces, then without loss of generality, the fluctuating force can be broken into a sum over different types of interactions:

$$L(t) = \sum_j \frac{f_j(t)}{m}$$

$$< L(t)L(t') > = \frac{1}{m}\sum_j < f_{j(t)}(t)f_j(t') >$$

Since cross terms $\langle f_i f_j \rangle$ $i \neq j$ would be expected to vanish. Thus, the friction coefficient should be the sum of the contributions from the various interactions.

At the crudest level, the friction coefficient should be a sum of contributions from x< b and x> b (i.e., forces coming from above vs. below the particle). Predicting dynamical friction is fraught with assumptions and specificity. For example, the piecewise parabolic potential lacks a definition of the spacings *b-a* and *c-a*. While we can estimate the curvatures of the field from assumed potentials, the distance from the minima to the point $x=b$ is a function of the separation between the interfaces. The separation is not known nor can it be expected to be constant. We also need to address the problem stated above that the surfaces are not homogeneous. Since our current aim is to be parsimonious with assumptions and general in scope, that endeavor is left for future work. None the less, the two contributions should scale with (i.e., should be roughly proportional to) the friction at the two interfaces. Thus, the reduced friction function

$$h_b \sim \frac{(r\beta_a + s\beta_c)}{\beta_a} = r + \frac{s\beta_c}{r\beta_a} \tag{3}$$

should be expected to be a function of the friction coefficient at the solid surface divided by the friction coefficient at the liquid interface. This is the second, less obvious, way in which the product well influences the rate of wetting.

Of course, the dynamical friction will vary across the gap (the attraction to the surfaces decreases with separation). If this dependence is expanded in a power series, the odd powers are seen to vanish by symmetry while the even powers do not. Thus, corrections rising from the simplistic result given above can be expected to be of second order in x.

However, the division of the dynamical friction into contributions from x< b and x> b (i.e., the “reactant” state and the “product” state) is only the crudest way to divide the fluctuating interactions that might be at play. We might break the forces into numerous interactions such as interactions with vapor phase molecules, liquid molecules trapped near $x=a$, liquid molecules adsorbed on the solid surface (near $x=c$), and the surface itself (which does not fit naturally into the tripartite piecewise parabolic potential). Since the solid is moving relative to the liquid, surface corrugations become a natural source of fluctuations. If we consider contributions from molecules in the adsorbed state, the problem becomes inherently nonlinear. If we confine ourselves to fluctuations arising from the corrugation of the surface, we still have a linear problem; however, the approach will vary with substrate. For example, is wetting a perfect crystal, the fluctuations would be expected to be periodic and a harmonic analysis might be more appropriate. But most coating substrates are not perfect crystals: glass is amorphous, steel is polycrystalline (with a grain structure), and most common polymeric substrates are only partially crystalline and may be polycrystalline. There is also the problem of activation energy. The original problem statement was reconciling how an activation energy for adsorption can depend on the product state. The work of adhesion is a macroscopic property that characterizes the attraction of a liquid to a surface. That certainly will have the effect of lowering the barrier to adsorption shown in figure 1. It will also affect the well depth at $x=c$. However, the effect of surface corrugations on thermal fluctuations in attraction to the surface is more likely to have an activation energy that scales with the binding energy of the solid than that of an adsorbed liquid.

Physisorbed molecules are likely to reflect the corrugations of the surface while experiencing a Boltzmann distribution in position that scales with the work of adhesion. Unfortunately, these questions are unresolvable within the current framework.

## **Conclusions**

The fundamental question under consideration is: how can an activation energy for adsorption depend on the energy of the adsorbed (product) state rather than the liquid (reactant) state? Here we have two answers to that question. The most obvious way is in dropping the height of the barrier separation reactant from product. The less obvious way assumes the process is governed by the high friction Kramers theory of chemical reactions and that the dynamical friction is determined by fluctuating interactions with both interfaces. In this later case, the interactions with the "solid" surface may be with the solid itself and may be with liquid physisorbed on the surface. In the spirit of Ockham's razor, these effects have been predicted using only the following assumptions:

1) The Thompson and Troian mechanism is taken as a framework to pose the question
2) The forces in the gap between liquid and solid is largely pairwise additive dispersion forces
3) The qualitative behavior can be elucidated using the piecewise parabolic potential.
4) The dynamics of the system can be modeled using Smoluchowski's diffusion equation (unmodified)
5) The barrier is high enough for the Kramers flux over population method to give a reasonable reflection of the behavior.
6) The fluctuations in the pairwise additive dispersion forces are uncorrelated (leading to simple additivity of contributions to the friction coefficient).

Much work needs to be done to produce concrete predictions and resolve the nature of the contribution from the solid / adsorbed liquid interface; however, these results have been generated with elementary asymptotic analysis. The next level of results will require numerical simulations and a level of empiricism that must be consigned to future work.

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