

High Friction Stochastic Theory of Wetting

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1. Introduction and problem statement

Blake and DeConninck (Blake 2011) raise the question of whether the Kramers theory of chemical reactions can be applied to the problem of dynamic wetting and explore links between Kramers theory and what is commonly called the Molecular Kinetics Theory of wetting (“MKT”). The purpose of this work is to reexamine this question in the context of mechanistic models of dynamic wetting somewhat different than the standard model of the MKT within the high friction framework attributed to Kramers.

The traditional illustration used to explain the MKT is that molecules hop along the surface as shown on the left side of figure 1.

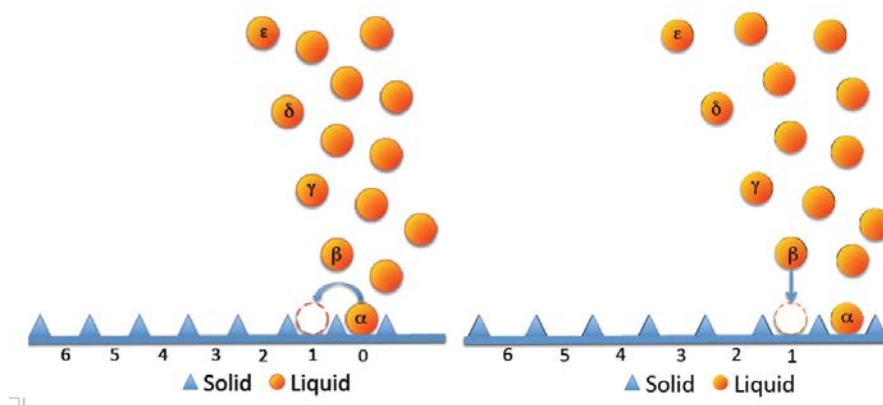


Figure 1 – Cartoon illustrations of dynamic wetting mechanism showing the in-plane transitions for the MKT (left) and out of plane transitions (right)

For continuous coating, the substrate would be moving from left to right at a constant speed determined by the mechanical drive system and the contact angle would depend on interactions between the liquid coating and the substrate along with the coating speed. For the case of a spreading drop, the liquid would be moving from right to left at a speed and with a contact angle that varies with time as the drop spreads.

The MKT uses transition state theory to model the rate of jumps in the location of the dynamic contact line. Transition state theory uses an assumed equilibrium between a “reactant state” and a “transition state” based on the partition functions of the reactant and transition states. Both Blake and Haynes (Blake 1969) and Cherry and Holmes (Cherry 1968) use equilibrium arguments to eliminate the partition functions but to do so requires limiting the mechanistic model of wetting to one of a molecule adsorbed to the surface “jumping” along the surface to a free site as shown. Many refinements have been

made to the MKT over the years (e.g., Duvivier, 2013); however, the importance of the work of adhesion in successful correlations to the contact line friction is highly suggestive that what are shown on the sketch as $\alpha \rightarrow 1$ transitions play a central role in wetting.

In contrast, the stochastic theories discussed here depend on the detailed molecular mechanism of wetting. Clearly any of the liquid molecules in the cartoon could be the next to adsorb to the surface and they may adsorb at any site on the surface. There may be a dominant transition such as the molecule labeled β being the most common precursor state to adsorption at site 1 (etc.). Certainly the relative rates of $\alpha \rightarrow 1$ transitions to $\beta \rightarrow 1$ transitions can be expected to vary with contact angle. From a molecular perspective the rate of wetting should be given by summing the rates at which molecules coming from any precursor state adsorb at any site on the solid surface. Thus, the scope of this talk is limited to presenting a general algorithm for computing the rate at which molecules in various positions on the liquid gas interface adsorb onto the solid surface and discussing what might be learned about dynamic wetting by studying the microscopic behavior of an ensemble of molecules behaving as Brownian particles in a field of force.

2. Background

H. A. Kramers (Kramers, 1940) proposed that the rate at which chemical reactions proceed along a one dimensional reaction coordinate could be modeled as Brownian motion with the interaction of the reactant moieties with the surrounding “heat bath” being expressed as a viscous resistance. The extensive review by Hänggi et al (Hänggi 1990) provides a comprehensive perspective on the use of the Kramers theory in modeling rate processes. Three salient points warrant repetition here. First, Kramers discusses three regimes of thermally activated processes: a low friction limit (in which the rate is proportional to the dynamical friction coefficient), a moderate friction case (which gives mild corrections to transition state theory results) and a high friction limit in which the evolution of the ensemble averaged density of particles is governed by the Smoluchowski equation. Second, dimensional analysis shows that rate constants from Smoluchowski’s equation must vary as the inverse of the dynamical friction coefficient. Since the dynamical friction coefficient scales with viscosity, the Smoluchowski limit is consistent with the empirical observation that the speed of dynamic wetting is inversely proportional to the viscosity. Thus, this initial foray into stochastic modeling of dynamic wetting begins with the Smolouchowski limit. Finally, Hänggi traces one of the boundary conditions used by Kramers back to Farkas (Farkas1927). Farkas assumed that the division between “reactant” and “product” states occurs at the top of the potential barrier separating the “reactant” and “product” potential wells. The mathematical implications of this intuitive assumption are discussed below.

Three general approaches have been used to estimate the rate of reaction for particles leaving a potential well in the case of high friction. Pontryagin et al (Pontryagin 1933) were the first to give a general solution to the mean time to escape from a potential well for the case of a potential barrier with a reflection condition at one side and an absorbing

condition at the other. This approach can also give the rate of passage over periodic potential barriers (e.g., surface diffusion); however, this approach has been limited to cases of constant friction coefficient. The second approach, attributed to Kramers is to calculate a pseudo steady state flux of particles passing over the barrier between reactant and product states from asymptotic solutions to Smoluchowski's diffusion and normalizing this to the total number of reactant particles to get a one way rate constant for escape. A third approach starts with the Smoluchowski equation but casts the problem as a Sturm Liouville problem for equilibration in a double well (Larson and Kostin 1978) and equates the first nonzero eigenvalue of this Sturm Liouville problem with the two way rate constant for equilibration in the double well. This Sturm Liouville approach is the primary approach used in the work presented here. Since the process of dynamic wetting involves a particle (e.g., a molecule) moving from a liquid phase through a region that may be a gas phase or may be a layer too thin to be called a "phase" into an adsorbed state, spatial variations in the dynamical friction coefficient may be significant. Thus, the approach followed here is based on a variable friction version of the Smoluchowski equation.

3. Solution to the Smoluchowski equation

In the limit of high dynamical friction β , the ensemble averaged number density of particles ρ at any given point along the reaction coordinate ξ is described by Smoluchowski's diffusion equation.

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

The reaction coordinate ξ is not in general associated with a simple geometric coordinate. For example, the surface jumps modeled by the MKT may not occur in the direction of spreading but may follow a contorted path that is defined by the minimum energy surface of particles adsorbed on a substrate. Thus, the coordinate of the one dimensional Smoluchowski equation should be viewed as a "reaction coordinate" not a Cartesian coordinate except in special cases. Smoluchowski's equation can be put in dimensionless form by introducing new variables

$$\begin{aligned} x &= \xi/\sigma \\ t &= \frac{k_B T}{m\beta_0 \sigma^2} \tau = \frac{D_0 \tau}{\sigma^2} \\ V &= \frac{E}{E_0} \\ c &= \rho \sigma \end{aligned}$$

where σ is the collision radius of the particle:

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

Here w is the number density per collision radius and $h(x) = \frac{\beta(x)}{\beta_0}$ accounts for spatial variations in the dynamical friction.

The formal substitution

$$w(x, t) = w_0 g(x) e^{-CV(x)} e^{-\lambda t}$$

defines the dimensionless rate constant λ and the depletion factor g . At equilibrium, the rate constant vanishes, g becomes unity and $w_0 e^{-CV(x)}$ is the Boltzmann distribution for the probability of finding a particle at dimensionless reaction coordinate x . In the non-equilibrium case, the depletion factor can be understood to represent the deviations from equilibrium (the Boltzmann distribution) caused by the flux of particles out of the well. The behavior of the depletion factor is governed by the differential equation

$$\frac{d}{dx} \left[\frac{1}{h(x)} e^{-CV} \frac{dg}{dx} \right] + \lambda e^{-CV} g = 0 \quad (1)$$

Two boundary conditions are then required to determine $g(x)$ and the choice of boundary conditions depends on the formalism being considered. For the Kramers approach, the first boundary condition is that the depletion factor vanish at some point, for the sake of convenience referred to as the annihilation point since particles that reach this point “vanish” (analogous to Pontryagin’s absorbing boundary). This point will be denoted by $x=A$. Farkas (1927) is generally credited with associating this annihilation point with the top of the barrier. The reasons for choosing this boundary condition warrant further discussion below. The choice of the second boundary condition is not as clear from a mathematical point of view. For the Sturm Liouville approach, one boundary condition must be at the solid surface and the natural choice of boundary condition is the “no-penetration” condition (i.e., that the flux goes to zero at the singular point in the potential that corresponds to a solid surface). It is easily shown that this reduces to a requirement that dg/dx vanish at the solid surface. The boundary condition at the liquid interface is somewhat less obvious. It is often assumed that equilibrium is attained at the bottom of the well representing the “reactant” state. This translates to g being constant at the bottom of the reactant well. Alternatively, since the value of the depletion factor at the liquid interface is only needed within an arbitrary multiplicative factor, for numerical purposes, the depletion factor can be assumed to take any convenient value at the liquid end of the range of x .

In general, this two point boundary value problem cannot be solved exactly; however, Lightfoot (1985) was able to find a general prediction of the leading behavior of the solution as C becomes large using the method of dominant balance (see, for example, Bender 1978). If the barrier to escape from the potential well is high, the only asymptotically consistent approximation to (1) is:

$$\frac{d}{dx} \left[\frac{1}{h(x)} e^{-CV} \frac{dg}{dx} \right] \approx 0 \quad (2)$$

This readily integrated to give

$$g(x) \approx \alpha \int_A^x h(x) e^{c\tilde{V}(x)} dx \quad (3)$$

thus,

$$w(x, t) \approx \alpha w_0 e^{-cV(x)} \int_A^x h(x) e^{c[\tilde{V}(x)]} dx e^{-\lambda t} \quad (4)$$

The explanation of the dominant balance arguments leading to equation (3) and (4) are left to longer communications (e.g., Lightfoot, 1985). For present purposes it suffices to say that in solving equations (2) and (3) care should be exercised to keep only terms of comparable order but also to keep all terms of comparable order.

4. Estimation of the rate constant

Kramer's method involves estimating the flux over the barrier from the solutions given above and dividing the flux by the number of particles in the well (evaluated by integrating over the entire well). The details are given elsewhere (Lightfoot 1985); however, the rate constant obtained this way is

$$\lambda \approx \frac{1}{h(A) \int_{x_0}^A e^{-cV(x)} \int_A^x h(x') e^{c[\tilde{V}(x')]} dx' dx} \quad (5)$$

The function $h(x)$ represents the ratio of the dynamical friction coefficient β at point x to the value at some reference point β_0 and the identification of $\tilde{V}(x)$ (see above). Lightfoot (Lightfoot 1985) chose the annihilation point $x=A$ as the reference point for dynamical friction in which case $h(A)$ is one.

The alternate approach to estimating the rate constant considered here is to associate the rate constant λ with the lowest non-zero eigenvalue of the Sturm Liouville problem defined by the differential equation (2) and two boundary conditions on g . As is well documented in standard textbooks on mathematics, Sturm Liouville problems of this type possess an infinite number of eigenvalues with associated orthogonal eigenfunctions. Any initial condition that possesses piecewise continuous first and second derivatives can be expanded in an absolutely and uniformly converging series of the eigenfunctions of the Sturm-Liouville problem. If the range of x is bounded by an annihilation point located at the top of a potential barrier, the zero eigenvalue (steady state solution) is that $g(x)=0$ for all x . This is not an interesting solution. Larson and Kostin (Larson 1978) consider the equilibration of particles caught in a symmetric double well as a Sturm Liouville problem where the range of x includes both "reactant" and "product" wells.

The approach that is taken here is to consider the wetting problem as a Sturm Liouville problem in an asymmetric double well: the "reactant" well would correspond to a

“particle” at some point on the liquid vapor interface (inclusive of the point labeled α in figure 1) while the “product” well would correspond to adsorption on the solid surface. There is no need to construct a mathematically reflected well; however, the location of the annihilation point is not known intuitively.

The lowest non-zero eigenvalue is associated with the rate constant and the eigenfunction associated with this eigenvalue must possess one zero. Moreover, the eigenfunctions of the Sturm Liouville problem are orthogonal when integrated over the range of x with the weighting function $e^{-CV(x)}$ in the sense that

$$\int_{x_1}^{x_2} g_i g_j e^{-CV} dx = 0 \text{ if } i \neq j$$

Consider the first two eigenfunctions. Since g_0 is a constant,

$$\int_{x_1}^{x_2} g_1 e^{-CV} dx = 0$$

and

$$\int_{x_1}^A g_1 e^{-CV} dx = \int_{x_2}^A g_1 e^{-CV} dx. \quad (6)$$

This gives a rigorous (but implicit) mathematical definition of the annihilation point that is independent of any intuitive assumptions about absorbing boundaries (that may not be physically realizable). Remembering that the asymptotic relationships (3) and (4) are based only on the depletion factor $g(x)$ vanishing at the annihilation point – not the derivative of the potential function vanishing—the estimate of g_1 should remain asymptotically valid.

There is relatively little that can be deduced about the function g_1 from equation (6) for an arbitrary potential function $V(x)$. For a potential that is symmetric about $x=0$, g_1 must be an odd function of x : $g_1(x) = -g_1(-x)$. Thus, equation (6) is satisfied identically for a symmetric double well. The boundary conditions for g_1 are that g is constant near the bottoms of the two well (certainly the boundary condition on the well representing adsorption on the solid surface might be enforced in the limit as x approaches the surface). Defining g^+ and g^- as the limiting constants in the two ends of the range, the ratio g^+/g^- can be found from

$$g^- \int_{x_1}^A e^{-CV(x)} dx \approx -g^+ \int_A^{x_3} e^{-CV(x)} dx$$

by noting that

$$\frac{\int_{x_1}^A e^{-CV(x)} dx}{\int_A^{x_3} e^{-CV(x)} dx} = K_{eq}$$

where K_{eq} is the equilibrium constant between the number of particles in the “reactant” and “product” states at equilibrium. Thus,

$$\frac{g^-}{g^+} \approx -K_{eq} \quad (7)$$

Equation (7) is valid in the limit where the barrier between “reactant” (surface of the liquid) and “product” (adsorbed on the solid surface) states is high enough for $g_I(x)$ to become asymptotically constant in the potential wells.

Unfortunately, it is difficult to extract information about the location of the annihilation point from (6) because the minimum in the weighting function occurs near the annihilation point (in the case of the Farkas condition, the annihilation point would be assumed to occur exactly at the minimum in the weighting function) and the eigenfunction g_I vanishes at the annihilation point by definition. Thus, equation (6) requires the difference between two numbers that are relatively insensitive to the behavior near the annihilation point to vanish; thus, the only hope of garnering information on the location of the annihilation point is to solve equation (6) with high precision. That requires the potential function to be sufficiently simple to allow analytic evaluation of the integral or an accurate numerical solution. It also points out the sensitivity to the location of the annihilation point and to the possibility that relatively subtle variations in the potential may move the annihilation point away from the top of the barrier. Here the significance of introducing the asymptotically consistent approximation \tilde{V} becomes clear: the asymptotic approximation of V to give \tilde{V} does not represent a license to ignore variations in the true potential, rather \tilde{V} represents a requirement that whatever approximations are made leave a potential energy function that is accurate over the range of variation in g_I .

5. Illustrative examples

The formalism outline above works equally well for any of the transitions shown in Figure 1. However, since these methods are intended to include mechanisms other than those normally associated with the MKT, it is useful to consider asymmetric double wells that involve dispersion forces such as asymmetric generalized Lennard Jones 3-6 double well described by as show

$$V = 2\left(\frac{1}{(-3+x)^6} + \frac{1}{(-3+x)^3}\right) + \frac{1}{(3+x)^6} - \frac{1}{(3+x)^3}$$

This is shown in figure 2.

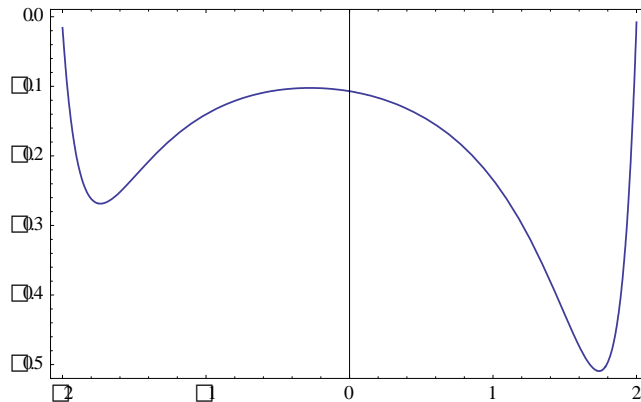


Figure 2 – Mildly asymmetric generalized Lennard Jones 3-6 potential double well

The choice of the r^{-6} repulsion from the liquid (shown at the left) is not realistic; however, the simplified form is sufficient for illustrative purposes. The r^{-3} terms should be qualitatively appropriate for attraction to the solid and liquid surfaces and the r^{-6} repulsion from the solid surface may be quite reasonable. The top of the barrier is in the left half plane; however, the weighting function is heavily skewed to the right half plane (shown with $C=5$).

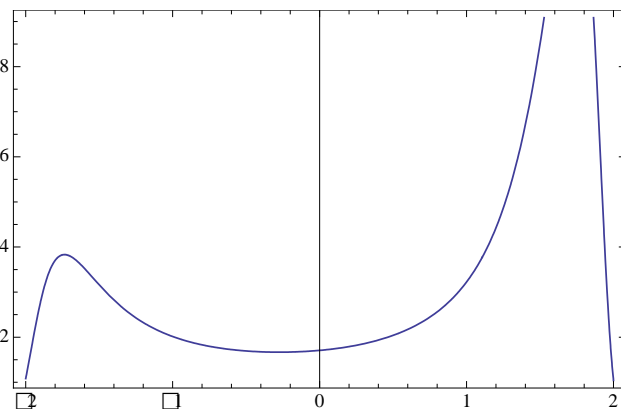


Figure 3 – Weighting function e^{-CV} for V as in Figure 2 and $C=5$

However, while the top of the well is in the left half plane, the zero of the eigenfunction (found by Mathematica) is in the right half plane:

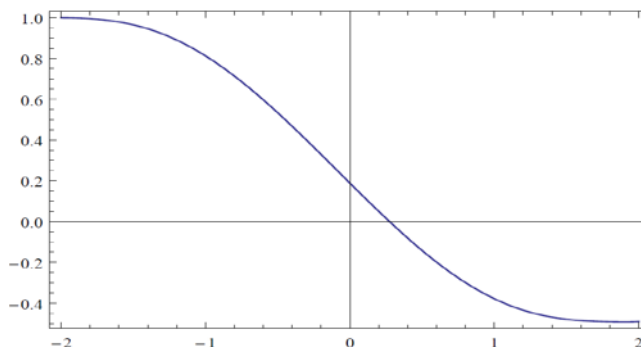


Figure 4 – Eigenfunction corresponding to the lowest nonzero eigenvalue

Remembering that the asymptotic expression for g_I is based on an approximation to the potential \tilde{V} that is accurate in the neighborhood of the annihilation point, the physical contrast between the Sturm Liouville approach and the Kramers approach becomes clear: while the Kramers approach focuses mostly on the reactant well the asymmetric Sturm Liouville approach shifts the focus more to the reactant well (for wetting, the adsorption to the surface). To be clear: both wells affect both theories, but the annihilation point shifting from the top of the barrier to the reactant well shifts the focus.

6. Toward a comprehensive theory of dynamic wetting

The stochastic algorithm for calculating the rate of individual transitions (using asymmetric Sturm Liouville problems) can be seen as a foundation on which a comprehensive theory of wetting might be built; however, stochastic theories of wetting cannot provide the same level of closure in predicting dynamic wetting speeds that the MKT offers. First, the eigenfunction that corresponds to the rate constant is negative in the “product” state. While one can expect to produce realistic rates for a given elementary reaction step with the Sturm Liouville approach, doing this requires looking at the sum of multiple terms (the addition of a small equilibrium component will avoid the issues with negative concentrations, but it may be that higher order –intrawell modes—are important as well). One must also account for advection. In the case of continuous coating, molecules that adsorb on the solid surface are carried away (under the meniscus) by the moving web. Finally, one must look carefully at the nature of a stochastic theory. The density function w (or ρ) represents the ensemble average density of particles at a given reaction coordinate. If this density represents less than full coverage of the surface at say position “1” on the cartoon in figure 1, some of the ensemble of sites “1” are not wetted—however as long as the density is greater than zero, some of the sites are wetted. If one does a population balance for the sites “0” in the cartoon, the “particles” (e.g., liquid molecules) that comprise the coating arrive at “0” by advection from site “1” as well as diffusion of molecules from the liquid phase – but assuming the ensemble of sites “0” are fully covered while the site “1” is not, the advection away from “0” will always exceed the advection to “0”. Furthermore, if site “0” is fully covered, the driving force for diffusion will be zero.

The resolution of the above conundrum is clear: stochastic theories of wetting cannot predict a sharp transition from “dry” to “wetted” substrate, however, they can, if suitably formulated, predict a gradual transition from wet to dry that might be useful for modeling precursor states.

Conclusion

This talk considers the question of what might be learned about dynamic wetting from stochastic theories of the type proposed by Kramers. Starting with a high friction analysis, it can be seen that dynamic wetting can be best modeled using a numerical Sturm Liouville formulation for the depletion factor g (which could be adapted to moderate friction behavior as well). However, stochastic models cannot provide predictions of the kinds of sharp transitions offered by the MKT. While the kinds of gradual transitions from dry to wetted predicted by stochastic models are appealing in

their qualitative agreement with experiments, kinetic models do not account for fluid mechanical effects and stochastic models may prove no more than a curiosity in the end. Furthermore, while the high friction Kramers theory offers an attractive starting point, this theory requires a number of physical assumptions that may not be valid for most coatings. However, Kramers theory is not the only stochastic theory that can be considered. Stochastic models provide hope for faster numerical methods than current Monte Carlo methods and show consistency with some known physical anomalies; thus, this emerging field must be viewed as offering significant promise.

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