Comparison of kinetic theories for modeling dynamic wetting

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Dynamic wetting is a complex phenomenon that is influenced by fluid mechanics as well as molecular level physics. While there is a consensus that a kinetic regime for dynamic wetting exists (Snoeijer 2013), there is not a clear consensus on the mechanism of the kinetics. The molecular kinetic theory (MKT) of wetting (Blake 1969, Cherry 1968) assumes the rate of wetting is given by the transition state theory (TST) expression for an interface moving by jumps along the surface—but retarded by a friction force. Blake and De Coninck (Blake 2011) introduce the idea that Kramers moderate to high friction model of escape for a piecewise parabolic potential (Kramers 1940) may apply to kinetic wetting. However, molecular dynamics (MD) simulations (e.g. Thompson 1997) using Lennard-Jones potentials show a liquid interface that is essentially parallel to the solid interface having a mean velocity different from that of the solid (i.e., a region of slip) until the particles get close enough to the surface to feel the corrugations of the repulsive potential. The topology of the MD model is more in keeping with fluid mechanical models for wetting.

This talk compares qualitative features of four theories that might be used to model kinetic wetting: transition state theory, the theory of reactive fluxes, the high friction Kramers theory and a high friction stochastic model based on Sturm–Liouville theory. The qualitative behavior of these kinetics theories depends on the potential energy function that is assumed (which, in turn, depends on the general mechanism that is assumed). These features are illustrated using two potential functions: the piecewise parabolic potential that gives rise to the TST theory result used in the MKT and a double well Mie potential that should be more appropriate for the mechanism seen in MD simulations.

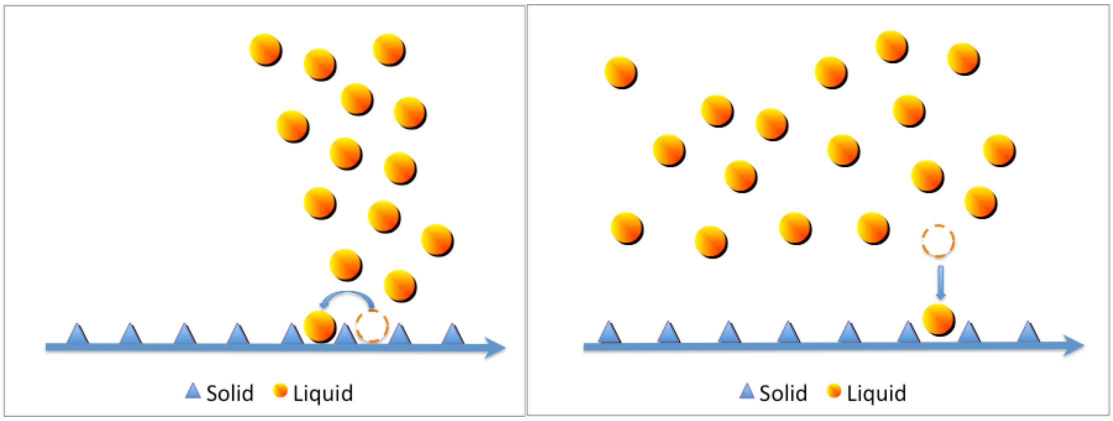

Figure 1 – Mechanism of dynamic wetting used for the MKT (left) and observed in molecular dynamics (right)

Potential functions

The most widely used approximation to the potential energy surface for a chemical reaction is the piecewise parabolic potential (PPP) approximation to a reactant well (near *x*=*a*), a barrier (near *x*=*b*), and a product well (near *x*=*c*)

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

$$E(x) \approx E(b) - \frac{(2\pi\omega_b)^2}{2}(x-b)^2\ ;\, x \approx b\ \text{(b>a)} \tag{1b}$$

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

Although discussions of the piecewise parabolic potential are often illustrated with continuous curves, the potential is only defined over two (1a, 1b) or three (1a, 1b, 1c) disjoint regions of the domain of the reaction coordinate *x*. This constrains the asymptotic approximations to the rate constant in ways that affect the physical picture that emerges. Nonetheless, this is the potential function on which most previous work has been based.

Calculating the potential energy of a particle desorbing from a liquid interface and adsorbing on a solid interface is a nontrivial exercise (see Israelachvili, 2011 for a general discussion) that is physically complicated by the possible presence of an air layer between the coating and the substrate. However, the Mie potential (Mie, 1903)

$$V(z) = -\frac{A}{(z)^n} + \frac{B}{(z)^m} \tag{2}$$

with n=3 represents the asymptotic approximation to the full Hamaker formula for the attraction of a particle to a surface in the same limit that gives rise to the inverse sixth power dependence of the Lennard Jones used in most MD calculations and is sufficient to illustrate the physics. Here *z* represents the distance from the interface. For computational purposes, the potential between the two surfaces is taken as the sum of Mie potentials acting from two surfaces taken to be at $x=\pm L$. The attractive terms are estimable from physics. The repulsive terms each have two adjustable parameters that can be used to fit the well depth and the curvature of the well at its minimum. The well depth at the liquid interface provides a connection with fluid mechanics since it is the energy of a molecule (or "particle") at a liquid surface that is being stretched and thus is related to the dynamic surface tension. The well depth at the surface is the binding energy of a single molecule adsorbed on the surface which is clearly different from but related to the work of adhesion (the energy of a bringing a continuous layer to the surface). A Mie double well is illustrated in figure 2.

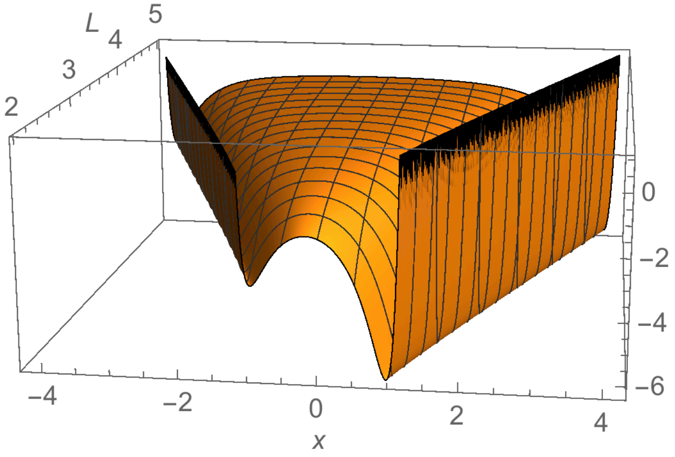

Figure 2 – Mie potential with n=3, m=9, A_l=5, A_s =10, B_l=3, B_s=6 with the liquid surface at x=-L and the solid surface at x=+L.

There are several significant features of the Mie potential. Unlike the piecewise parabolic potential, the Mie potential is continuously defined over the physical domain. However, the Mie potential diverges at the two surfaces bounding the physical region of interest. While the barrier looks parabolic for small separation, it is not well represented by a parabola for significant separation; thus finding a uniform approximation to the rate constant will be challenging. As the separation becomes large, the region between the surfaces becomes asymptotically flat (force free). Because the "barrier" arises as a balance of two long-range attractive forces, the barrier height drops as the two surfaces approach each other and the maximum in the potential is shifted toward the shallower well.

Reaction rate theories

The intent here is to discuss qualitative features of four well-known rate expressions for passage of a Brownian particle passing over a barrier. For derivations of the expressions and explanations of the theory see Hänggi et al (Hänggi 1990) or Schuss (Schuss 2013).

The TST theory for the PPP assumes an equilibrium between "reactant" molecules $(x \approx a)$ and molecules at the top of the barrier $(x \approx b)$. In terms of the potential (1), the transition state theory gives the rate of escape over the barrier as

$$k = \frac{\omega_a}{2\pi} e^{\left((E(a)-E(b)) / k_B T \right)} \tag{3}$$

This represents the maximum rate of passage assuming all molecules reaching the transition state pass over the barrier into the product state; however, the actual rate of passage may be less than the maximum rate by a "transmission factor" κ.

Kramers (Kramers, 1940) presents three stochastic theories for escape from a potential well that are asymptotically valid in the limits of low, high and moderate values of the dynamical friction coefficient using a flux over population approach to estimate the rate constant in the three regimes for two potentials. In the moderate to high friction regime, Kramers estimates the rate constant for the PPP to be

$$k = \left[\left[\frac{\gamma^2}{4} + {\omega_b}^2\right]^{1/2} - \frac{\gamma}{2}\right]\frac{\omega_a}{2\pi\omega_b}e^{\left(E(a)-E(b))/_{k_BT}\right)} \tag{4}$$

Here γ is a damping coefficient identified by Kramers as the viscosity and by others as the dynamical friction (that scales with viscosity). This is the kinetic expression considered by Blake and de Connick (Blake, 2012). In the limit of zero friction, this parabolic barrier Kramers theory ("PKT") reduces to the TST result used in the original MKT, while in the limit of high friction ($\gamma >> \omega_b$) this asymptotically approaches the Smoluchowski result considered by Davitt (Davitt 2013)

$$k = \frac{2\pi\omega_a\omega_b}{\gamma}e^{(E_a-E_b)/_{k_BT}} \tag{5}$$

that was also given by Kramers (although previously derived by others as discussed by Hänggi). Because the viscosity scales with the dynamical friction coefficient, the high friction limit is consistent with the empirical observation that the speed of wetting is inversely proportional to the viscosity of the liquid. This parabolic Smoluchowski limit (PSL) may work for the Mie potential at low separation; however as the separation becomes large, ω_b goes to zero and (5) ceases to be useful.

Although the Kramers theory has a stronger dependence on the shape of the barrier than TST, the details of the product well are as irrelevant in the PKT and PSL as they are in the TST. Since the TST used in the MKT depends only on the curvature of the reactant well and the barrier height (activation energy), the observation that the contact line friction is best correlated to the work of adhesion, the mechanism for surface jumping sketched on the left side of figure 1 makes intuitive sense: if the activation energy scales with the work of adhesion, the reactant must be adhered to the surface. However, as discussed below, other theories take the shape of the product well into account.

While the TST and PKT are models for one way reactions (i.e., escape from a "reactant" well over a barrier), the "reactive flux" theory models the rate at which fluctuations (deviations from equilibrium) are dissipated. Equilibrium involves a significant population of particles in both reactant and product wells and the theory tracks the rate at which particles move from well to well with a Heavyside step function θ (defined such that θ is zero in the reactant well and unity in the product well). This theory can be used to model short-term dynamics; however, the result of current interest is the long time asymptotic behavior (e.g., Chandler 1982). Over long enough time scales the fluctuations decay exponentially with a time constant τ_{rxn} given by

$${\tau_{rxn}}^{-1} = k_{Overall} = k_+ + k_- \tag{6}$$

The rate of dissipation of a fluctuation is equal to the sum of the forward and the backward rate constants. Thus, even for the TST and PKT, the shape of both the reactant and product wells affects the relaxation time. However, if one rate constant is much larger than the other, the faster rate process will largely govern the relaxation behavior.

The final theory to consider is the Sturm–Liouville approach to solving Smoluchowski's diffusion equation first proposed by Larson and Kostin (Larson 1978) and applied to Mie potentials with m=2n by Lightfoot (1985). Details can be found in (Larson 1988). Because that theory is the source of the original insights being presented here, a bit more background is in order.

In the limit of high dynamical friction the density of particles at any given point along the reaction coordinate is described by Smoluchowski's diffusion equation (shown here for constant friction in dimensionless form):

$$\frac{\partial w}{\partial t} = \frac{\partial}{\partial x}\left[\left(\frac{\partial w}{\partial x} + \frac{dV}{dx} w\right)\right] \tag{7}$$

The formal substitution

$$w(x,t) = \ w_0 g(x) e^{-V(x)} e^{-\lambda t} \tag{8}$$

defines the depletion factor *g*. Setting λ to zero and *g* to a constant gives the Boltzmann distribution for the probability of finding a particle at reaction coordinate x. In the non-equilibrium case, variations in the depletion factor represent variations from equilibrium that govern the flux of particles. The depletion factor is governed by the differential equation

$$\frac{d}{dx}\left[e^{-V}\frac{dg}{dx}\right] + \lambda e^{-V} g = 0 \tag{9}$$

If the boundary conditions are of standard form, the problem becomes a regular Sturm-Liouville problem. The first non-zero eigenvalue λ_1 is associated with the rate constant. Higher eigenvalues are associated with intra well modes. For the general double well problem, the boundary conditions in each well become Neumann conditions (*dg/dx=0*) and the Rayleigh quotient

$$\lambda_1 = \frac{\int_{x_1}^{x_2}\left[\frac{dg_1}{dx}\right]^2 e^{-Cv}\, dx}{\int_{x_1}^{x_2} {g_1}^2\, e^{-Cv} dx} \tag{10}$$

can be used with an estimate of the eigenfunction accurate to order ε to produce an estimate the eigenvalue with an error of order ε^2 (e.g. Lightfoot 1985). For symmetric wells, symmetry guarantees *g=0* at the mid point and the domain can be halved.

The physical constraint that concentration cannot be negative puts a minimum bound on the coefficient of the eigenfunction corresponding to the equilibrium solution. An upper bound for the driving force is defined for the limit of zero concentration in the product well (not the transition state) while ignoring the intra well relaxation modes. From equation (8) the constraint c≥0 is equivalent to g ≥ 0. Since g_1 changes sign the physical constraint requires $g_0 \geq -g_1(x_2)$; thus, the one way rate constant k_+ is

$$k_+ \approx \lambda_1 \frac{g_1(x_1)}{g_1(x_1) - g_1(x_2)} \tag{11}$$

For symmetric potentials (e.g., Larson, 1978) k_+ is one half the eigenvalue.

In general, this two point boundary value problem cannot be solved exactly; however, the equilibrium solution is trivial and an asymptotic approximation to the eigenfunction corresponding to the first nonzero eigenvalue ($g_1(x)$) when the wells are deep can be found (Lightfoot, 1985) using the method of dominant balance (Bender 1978). The key to this solution is to recognize that the eigenfunction corresponding to the first non-zero eigenvalue has exactly one zero on the domain of x (defined as x_0). The leading behavior is then given in terms of an asymptotically consistent approximation to the potential function

$$g_1(x) \approx \alpha e^{\tilde{V}(x_0)} \int_{x_0}^{x} h(x) e^{[\tilde{V}(x) - V(x_0)]} dx \tag{12}$$

For the symmetric case, g_1 vanishes at the origin by symmetry; for the asymmetric case the point x_0 is determined by the orthogonality condition on the eigenfunctions corresponding to the two lowest eigenvalues. The eigenfunctions of the Sturm Liouville problem are orthogonal when integrated over the range of x with the weighting function $e^{-V(x)}$ in the sense that

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

Since g_0 is a constant

$$\int_{x_1}^{x_2} g_1 e^{-V} \, dx = 0.$$

Thus

$$\int_{x_1}^{x_0} g_1 e^{-V} \, dx = \int_{x_2}^{x_0} g_1 e^{-V} \, dx \tag{13}$$

gives a rigorous, if implicit definition of x_0.

Some care must be taken to apply (12) in an asymptotically consistent manner. To identify the correct leading behavior of the solution only terms of comparable order should be kept. In particular, if $g_1(x)$ varies over a narrow range of x, then the terms that are negligible over that range of x should be discarded. On the other hand, terms that are significant over that range of x should not be discarded.

This method is best illustrated using the potential defined in equation (1). Given the disjoint nature of the PPP, 1a, 1b and 1c give $\tilde{V}$ for the three regions. The only meaningful limit assumes the barrier (1b) is high enough and remains parabolic over a sufficient range of *x* that the eigenfunction reaches asymptotically constant values that are extrapolated into each well. For deep wells, the orthogonality condition is dominated by the integrals in the wells and the asymptotic limits for the eigenfunction come from the barrier region by extending the integrals from *a* to -∞ and from *c* to ∞. The integrals can then be expressed in terms of complementary error functions and x_0 can be found from the orthogonality condition.

$$x_0 = \frac{erfc^{-1}\left(\frac{2e^{V_c}\omega_c}{e^{V_a}\omega_a + e^{V_c}\omega_c}\right)}{\sqrt{2}\pi\omega_b}$$

(14)

If the problem is symmetric then $V_a = V_c$ and $\omega_a = \omega_c$ and $x_0=0$ since erfc(0)=1. However, asymmetric double wells can give $x_0=0$, if

$$\frac{\omega_a}{\omega_c} = e^{V_c - V_a}$$

(15)

Remembering that V is a dimensionless energy $=E/k_BT$, if the deeper well is also flatter there will be a unique temperature for which $x_0=0$. Although the zero of the eigenfunction is often not at the top of the barrier, after considerable algebra the Rayleigh quotient reduces to

$$\lambda_1 = 2\pi\omega_b e^{-V_b}(\omega_a e^{V_a} + \omega_c e^{V_c}) = k_+ + k_-$$

(16)

This is as predicted by the theory of reactive flux for the PSL. The ratio of the asymptotic values in the two wells is

$$\frac{g_a}{g_c} = 1 - \frac{2}{erfc(\sqrt{2}\pi x_0 \omega_b)}$$

(17)

which can be substituted into (7) to reveal that the one way rate constant reduces to the PSL result (5). Note that k_+ is expressed in dimensionless form while k in (5) is not.

The significance of this is its consistency with previous work and documenting the assumptions needed to derive it. Substituting (12) substituted into (10), x_0 does not enter into the numerator and only affects the denominator of the if nonzero x_0 leads to variations in g_1 in the wells. Because of the disjoint definition of the potential function and the assumption that the eigenfunction is assumed constant in the wells, although the values are different; the approximate eigenfunction is as binary as the Heavyside step function used in the theory of reactive flux.

Turning to the Mie potential, the only known formulae for escape rates from Mie potentials (Lightfoot, 1985, Larson, 1988) are for the special case of *m=2n* (Lennard-Jones type potentials) with well depth ($C=E/k_BT$)>>1 but at a large enough distance from the surface that CL^{-n}<<1. Accurate evaluation of the asymptotic series given requires some subtlety; however, the basic physics can be illustrated by taking the first term in the series. For both the Kramers approach and the Sturm-Liouville approach, the rate constant for escape with *g(L)* set to zero is approximately

$$k \sim \left(\frac{C}{\pi}\right)^{1/2} \frac{n 2^{-1/n} e^{-C}}{L - (4C)^{1/n} \Gamma\left(1 - 1/n\right)} \tag{18}$$

The rate constant exhibits the normal Arrhenius dependence; however, the pre-exponential factor has an unusual dependence. As L becomes large, the rate of escape goes as $1/L$ – consistent with the picture of most of the molecules being in the well and the few in the flat region of the potential diffusing at a more or less steady state between the well and L; however, the effect of the well on the pre-exponential term is negative—the reactant well essentially giving the particles a "head start" in diffusing away from the surface. The deeper the well, the higher the pre-exponential term. The effect of the activation energy is discussed below.

The Kramers approach to predicting the rate constant involves finding a pseudo-steady state concentration and flux. If the separation is large enough that that the two wells do not interact, the eigenfunctions for the single well problem (that disappear at $x=L$) might be adaptable for the double well case; however, the point x_0 would not necessarily be expected to fall at the origin (see equation (14) for the PPP) but can be estimated from (13). However, there are other cases of interest in looking at the double well Mie problem. If the mechanism of dynamic wetting is as revealed by MD simulations (sketched on the right hand side of figure 1), the liquid and solid interfaces begin at large separation and with relatively deep wells would exhibit exponentially small rates of mass (and momentum) transfer described qualitatively by equation (18). However, as the interfaces approach each other, the separation may not be sufficient to warrant the assumption $CL^{-n} \ll 1$ used to derive (18). As the interfaces get yet closer, the barrier gets lower and the deep well assumptions may no longer be reasonable. As the wells get shallower, the rate of motion may no longer be exponentially small and the majority of the mass transfer may come when the two interfaces are close together. Although there are many tools for developing asymptotic solutions in these various cases, the prospect of finding a simple formula that applies uniformly across the regimes seems remote.

The simplest way to look at the physics of a Mie double well at low separation is numerical solution to (9). Figure 3 shows numerical result for x_0 for the 3-hard sphere potential (i.e., numerical approximations for g_1 for $V(x) = \tilde{V}(x)$) with the liquid and solid surfaces at x =-2.5 and +2.5. Remembering that the maximum of the potential is skewed toward the shallower well, the distance Δ between the maximum and x_0 is considerably larger than x_0 and is shown in figure 4. This would further skew the effect on the pre-exponential term in (18), however, if x_0 falls in the deeper well, the activation energy is also reduced. Comparing the magnitude of x_0 to L in figure 3 it is clear that x_0 falls in the well representing adsorption to the solid surface.

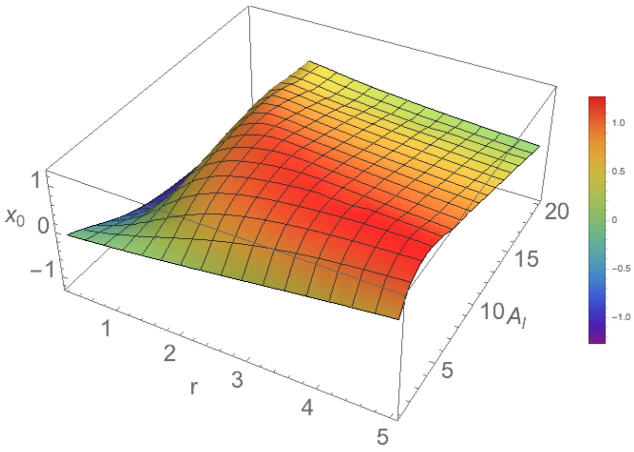

Figure 3 - Zeroes of the eigenfunction g_l for the 3-hard sphere potential with $A_s=rA_l$ and the liquid interface at $x=-2.5$ and the solid interface at $x=2.5$.

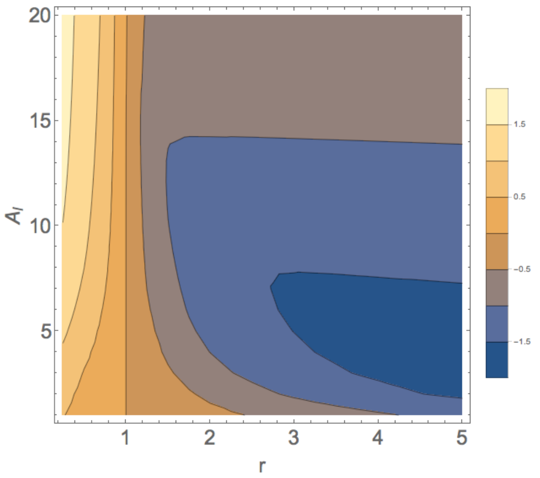

Figure 4 – Distance between the maximum and x_o for the same potential as Figure 3.

Summary

The MKT is a concise theory given in terms of measurable properties that provides the best correlation to data on kinetic wetting available today (DuVivier 2013). The molecular mechanism used in the MKT is suggested by TST and any other theory that relies on the activation energy being the difference between the bottom of the reactant well and the top of the "barrier" since, as seen from the theory of reactive fluxes, the fastest one way rate constant should dominate the overall relaxation rate. Nonetheless, the molecular mechanism assumed in the MKT is in conflict with MD simulations. The Sturm-Liouville approach to solving Smoluchowski's equation shows two mechanisms by which the attraction to the solid interface can accelerate the rate constant for the backward reaction (an increase in the pre-exponential factor and a decrease in the activation energy as x_0 moves closer to the surface) provided the mechanism of wetting is as shown from MD simulations. However, while Sturm-Liouville theory shows promise, much work remains to be done before it provides a useful correlation.

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