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The molecular-kinetic approach to wetting dynamics: Achievements and limitations

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ABSTRACT

The molecular-kinetic theory (MKT) of dynamic wetting was formulated almost 50 years ago. It explains the dependence of the dynamic contact angle on the speed of a moving meniscus by estimating the non-hydrodynamic dissipation in the contact line. Over the years it has been refined to account explicitly for the influence of (bulk) fluid viscosity and it has been applied successfully to both solid–liquid–vapour and solid–liquid–liquid systems. The free energy barrier for surface diffusion has been related to the energy of adhesion. The MKT provides a qualitative explanation for most effects in dynamic wetting. The theory is simple, flexible, and it is widely used to rationalize the physics of wetting dynamics and fit experimental data (dynamic contact angle versus contact line speed). The MKT predicts an intermediate wettability as optimal for high-speed coating as well as the maximum speeds of wetting and dewetting. Nevertheless, the values of the molecular parameters derived from experimental data tend to be scattered and not particularly reliable. This review outlines the main achievements and limitations of the MKT and highlights some common cases of misinterpretation.

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1. Introduction

The static wettability of solid surfaces is well-understood [1–4]. The major emphasis is the contact angle and its close relation to the interfacial interactions as captured in the famous Young's equation:

$$\gamma_{SV} - \gamma_{SL} = \gamma \cos \theta_Y \quad (1)$$

where γ_{SV} , γ_{SL} , and γ are the solid–vapour, solid–liquid and liquid–

liquid interfacial tensions, respectively. The main deficiency of Eq. (1) is that it predicts a single-valued equilibrium contact angle, θ_Y , and this is almost never the case. In practice a significant contact angle hysteresis is usually present and must be dealt with.

A separate problem arises when the contact line is moving. In experiments a dynamic contact angle, θ , is often measured with a reasonable reproducibility (Fig. 1). Under dynamic condition the main dissipation mechanisms must be identified in order to build a model. The MKT takes a microscopic view of the contact line [5–7]. All liquid molecules are in thermal motion including those in the vicinity of the contact line. Microscopically the contact line oscillates due to molecular jumps in random directions but on the average it remains macroscopically static. When an external force is applied, the forward direction of

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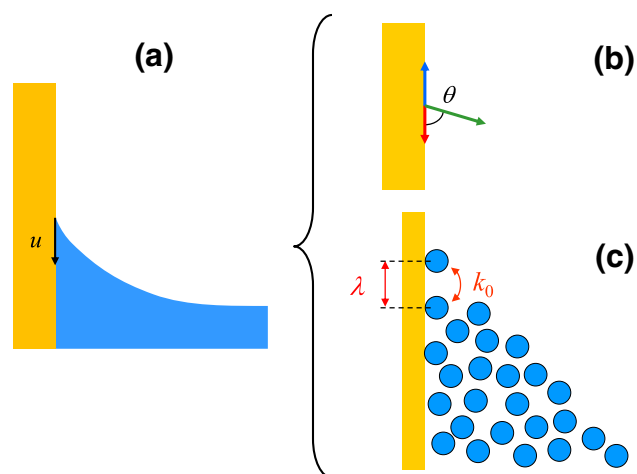


Fig. 1. (a) A macroscopic meniscus at a vertical wall moving at speed, u , with respect to the solid surface; (b) the tangential balance of interfacial tensions that provides the driving force for contact line movement; (c) molecular-kinetic picture of the dynamic contact line (k_0 and λ are the molecular parameters).

molecular movement becomes energetically preferred and the contact line drifts forward. This movement is registered on the macroscopic scale.

According to the MKT the dissipation of energy arises from the molecular movements and is localised near the contact line [5–7]. The small changes in the barriers to movement (decrease in the forward direction and increase in the back direction) are treated within the reaction rate theory originally developed by Eyring and co-authors.

The approach is based on Eyring's scheme for treating transport phenomena [8] and provides a relatively simple model which has achieved significant popularity. Wetting dynamics is a key topic that is relevant in various situations. Some of these, like the speedy coating of polymer substrates, have lost their industrial relevance but in other cases the interest is continuing or newly expanding. An example of the former is froth flotation [9], where the expansion of the contact line over the valuable particle is fast, poorly understood, and certainly of utmost importance. In micro- and nanofluidics, the capillary filling of channels is a fundamental aspect of various miniaturised devices. A recent review [10] of the applicability of Washburn's equation at the nanoscale crucially asked the question of the behaviour of the dynamic contact angle and currently there is no definitive answer. It therefore seems appropriate to review the achievements and limitations of the molecular-kinetic approach.

The structure of the review is mapped in Table 1.

Table 1
Table of contents.

Derivation	The original Blake–Haynes equation is derived by considering the unbalanced Young force and the molecular dissipation using Eyring's approach.
The role of viscosity	The role of bulk viscosity is well-documented experimentally but was ignored in the original MKT. Recent developments related to solid–liquid–liquid systems are examined.
The role of adhesion	The energy of adhesion is closely related to the activation energy of the adsorption–desorption process. The optimum wettability for the fastest coating is discussed.
Heterogeneous surfaces	The adaptation of the MKT to heterogeneous solid surfaces is reviewed.

2. Derivation

The driving force for contact line movement is the unbalanced Young force [2]:

$$f_Y = \gamma_{SV} - \gamma_{SL} - \gamma \cos \theta \quad (2)$$

where γ_{SV} , γ_{SL} , and γ are the interfacial tensions of the solid–vapour, solid–liquid and liquid–vapour interfaces, and θ is the dynamic contact angle. If the dynamic contact angle is equal to the equilibrium contact angle, θ_0 , the unbalanced Young force is zero and we obtain the Young Eq. (1). The Young equation can be used to write the driving force as

$$f_Y = \gamma(\cos \theta_0 - \cos \theta). \quad (3)$$

The driving force is positive when it drives the contact line further over the solid surface and negative if it makes the contact line recede from the solid surface. Many authors consider the spreading coefficient [2], $S = \gamma_{SV} - \gamma_{SL} - \gamma$, which is essentially identical to Eq. (3) with $\theta = 0$. It is clear from Eq. (3) that we consider the difference between the dynamic contact angle and the equilibrium contact angle. In other words, the hysteretic range is excluded from these considerations. This is highly inconvenient as in practice one observes an advancing contact angle, θ_A (the largest static contact angle after the liquid has advanced over the surface) and a receding contact angle, θ_R (the smallest static contact angle after the liquid has receded from the surface). It is widely accepted that the driving force that should be considered in the advancing and receding case is

$$f_{A,R} = \gamma(\cos \theta_{A,R} - \cos \theta). \quad (4)$$

Traditionally the dynamic contact angle is regarded as a separate problem from the (static) contact angle hysteresis [7].

In the original molecular-kinetic theory [5] the dissipation occurs at the contact line only. Its magnitude is calculated based on Eyring's absolute rate reaction theory (or transition state theory), and more specifically on its application to transport phenomena [8]. Here we outline briefly this scheme.

In the microscopic picture of the liquid meniscus all molecules are in random thermal motion. The interfaces and the contact line are the statistical average locations. The molecules at the very end of the meniscus form the contact line – Fig. 1. These molecules are located in an energetic well (Fig. 2) and they move randomly forward (frequency k_+) and back (frequency k_-). In the absence of any external force the probabilities are equal so that, macroscopically, the contact line remains static. The key notion from the reaction rate theory is that the rate of

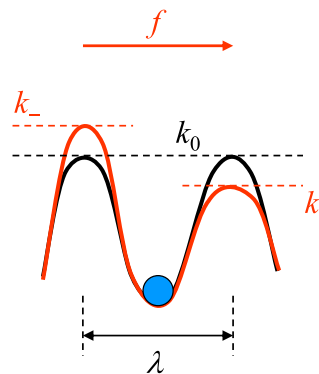


Fig. 2. Energetic landscape: (i) without any external force (black line) and (ii) under an external force f (red line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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