
On the microscopic parameters at a moving contact line during wetting process

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Abstract: The velocity of wetting a droplet on solid surface is a function of dynamic contact angle formed at a point on the contact line of solid and liquid phases. In this paper, the velocity of wetting obtained using the Arrhenius empirical equation is related to that of the dynamic contact angle. The resulting relationship, however, introduces two microscopic parameters, namely microscopic displacement frequency and length, which are not known a priori and are usually obtained using a curve-fitting of the measured data. A general correlation for the microscopic displacement frequency which has a wide range of variations is developed that is only a function of the known values of a wetting process. This correlation is presented by improving the available correlation for the surface component of the specific activation free energy of a wetting process using a curve-fitting of a wide range of experimental data. The predicted values from the correlation are in good agreement with those of the reported experiments even when a rough estimate value for the microscopic displacement length is used.

Keywords: contact angles; contact line velocity; wetting process; Arrhenius empirical equation.

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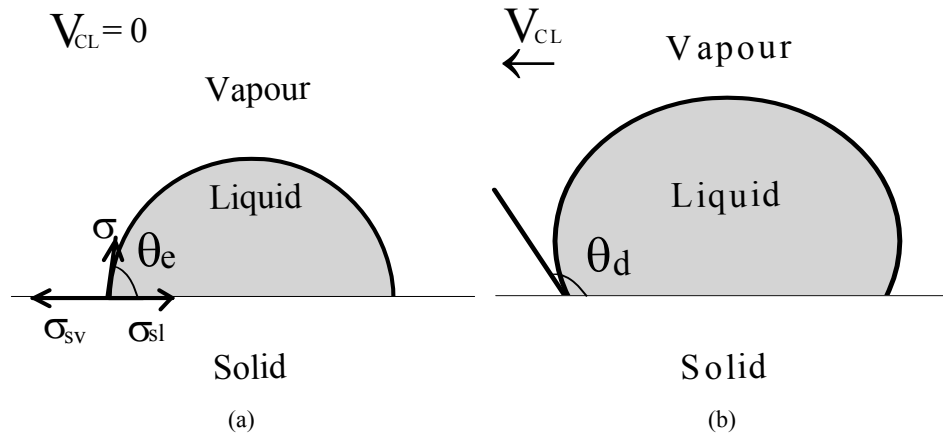
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1 Introduction

The dynamic wetting phenomenon of liquids on solid surfaces is discussed in a number of engineering applications such as thermal spray coating, spray cooling, paint spraying, ink-jet printing, petroleum recovery and distillation, and handling of liquid fuels in microgravity. In many of these technologies, the surface wetting effects during the impact of liquid droplets on a substrate play a crucial role in the system performance (Pasandideh-Fard et al., 1996). As a result, wetting dynamics has been the topic of many studies over the past decades (Pasandideh-Fard et al., 1996; Cherry and Holmes, 1969; Lopez and Miller, 1976; Foister, 1990; De Ruijter and De Coninck, 1997; De Ruijter et al., 1999; De Ruijter et al., 2000; Seveno et al., 2010; Petrov et al., 2003a; Roux and Cooper-White, 2004); in particular, the wetting of liquid drops on solid surfaces has been extensively studied (Šikalo et al., 2005a; Bayer and Megaridis, 2006; Lim et al., 2009; Xiaodong et al., 2007; Roisman et al., 2008; Wang et al., 2009; Bonn et al., 2009; Blake et al., 1999; Blake and Shikhmurzaev, 2002).

The equilibrium and dynamic wetting phenomena are introduced schematically in Figure 1 where a sessile drop on top of a substrate is shown in the two cases. A wide range of technological processes (e.g., cleaning, dyeing or gluing) depends on how well the liquid wets the surface of the solid material. This ability is quantified by the value of the equilibrium contact angle θ_e formed at a point on the contact line of solid and liquid phases by the tangents to the curves obtained by intersecting a plane perpendicular to the line of contact (Figure 1).

Figure 1 Wetting phenomenon in, (a) equilibrium state characterised by equilibrium contact angle θ_e (b) dynamic state characterised by contact line velocity V_{CL} and dynamic contact angle θ_d



The equilibrium condition, described by Young’s equation, can be stated as:

$$\sigma \cos \theta_e = \sigma_{sv} - \sigma_{sl} \tag{1}$$

where σ , σ_{sv} and σ_{sl} are the interfacial tensions at the three interfaces of liquid-vapour, solid-vapour, and solid-liquid, respectively. In the derivation leading to the above equation, the solid surface is assumed to be smooth, homogeneous, isotropic and non-deformable (Šikalo et al., 2005a). As seen from equation (1), the equilibrium contact

angle (θ_e) depends on the three interfacial tensions and is measured in complete static state of droplet on the substrate (Pasandideh-Fard et al., 1996). θ_d , displayed in Figure 1(b), is the angle formed between the moving liquid interface and the solid surface at the line of the three-phase contact (the contact line). Unlike the equilibrium contact angle, the dynamic contact angle is not only a material property; it is a function of the moving contact line velocity (Šikalo et al., 2005b) and also sensitive to the entire flow field near the wetting line (Shikhmurzaev, 1993). In many wetting scenarios such as droplet impact, the dynamic contact angle (θ_d) as a function of contact line velocity (Bayer and Megaridis, 2006; Roisman et al., 2008), should be used as a boundary condition to obtain better quantitative agreement of numerical predictions with experimental data. The spreading of a drop on a solid surface is a non-equilibrium phenomenon. It was described qualitatively by Brochard-Wyart et al. (1991) through an introduction of a spreading coefficient for wetting as:

$$S = \sigma_{sv} - \sigma_{sl} - \sigma \quad (2)$$

Complete wetting is obtained when $S \geq 0$ and partial wetting when $S < 0$. The case $S = 0$ is expected for very dry surfaces. The advancing angle is the largest contact angle observed before the wetting line begins to move in the direction of the vapour phase (also known as the wetting process) and the receding angle is the smallest contact angle achievable (also known as the dewetting process) before the wetting line begins to move in the direction of the liquid phase (Šikalo et al., 2005b). Extensive experimental studies on the wetting phenomenon are available in the literature (Foister, 1990; De Ruijter et al., 2000; Petrov et al., 2003a, 2003b; Roux and Cooper-White, 2004; Šikalo et al., 2005a; Bayer and Megaridis, 2006; Xiaodong et al., 2007; Petrov and Petrov, 1992a; Hayes and Ralston, 1993; Schneemilch et al., 1998; Drelich et al., 2002; Phan et al., 2003, 2006; Ranabothu et al., 2005; Vega et al., 2007). One of the main objectives intended in these experiments has been to understand the phenomena occurring in the vicinity of the moving three-phase contact line (Foister, 1990; Petrov et al., 2003a; Bayer and Megaridis, 2006; Vega et al., 2007). Although the wetting has been studied for many years, many fundamental problems are still open, especially those related to the motion kinetics of the contact line. In particular, the droplet impact phenomenon has attracted research interests since the 19th century, and it continues drawing attention due to its extensive industrial applications in various techniques (Roux and Cooper-White, 2004; Šikalo et al., 2005a, 2005b; Bayer and Megaridis, 2006; Wang et al., 2009; Bonn et al., 2009; Fujimoto et al., 2000; Werner et al., 2007). Many numerical and analytical studies (Pasandideh-Fard et al., 1996; Roisman et al., 2008; De Gennes, 1985; Liang et al., 2010; Blake et al., 1995; Xiaodong et al., 2003; Petrov et al., 1999; Chuang et al., 2009) discussed the spreading phenomenon of liquid particles on a solid surface. The simulation and prediction of such flows is still a challenging problem due to the existing numerical difficulties such as the need for an accurate modelling of the dependence of the contact angle on the contact line velocity (Bayer and Megaridis, 2006; Roisman et al., 2008). An accurate description of fluid flow at the liquid-solid-vapour contact line is important in formulating realistic models of droplet impact. Modelling fluid behaviour in the vicinity of a moving contact line is complicated, because assuming a no-slip boundary condition at the solid-liquid interface leads to a force singularity at the contact line (Pasandideh-Fard et al., 1996). The problem can be resolved by replacing the no-slip boundary condition with a slip model (Bayer and Megaridis, 2006). Though this method

alleviates mathematical difficulties, there is no experimental evidence to determine which of several available slip models is the most appropriate one to use. Numerical models of droplet impact usually specify the contact line boundary condition by assigning a value to the angle between the solid surface and the liquid/vapour interface (Pasandideh-Fard et al., 1996; Šikalo et al., 2005b). This apparent contact angle defines the shape of the free liquid surface above the contact line. The contact angle can, in principle, be measured directly from experiments and be used in the numeric model (Pasandideh-Fard et al., 1996; Fukai et al., 1995; Bussmann et al., 1999). Thermodynamic aspects of wetting and contact angles are generally well understood, but microscopic aspects are not. Energy dissipation during a contact-line spreading on a solid surface can be attributed to various mechanisms. If the leading contribution to the dissipation is due to the adsorption and desorption of molecules within the three-phase zone, then the molecular kinetic theory (MKT) best describes the wetting phenomenon (Blake and Haynes, 1969). However, if the viscous effect is the main factor in dissipating energy near the contact-line, the hydrodynamic theory should be used (Cox, 1986). A combination of molecular and hydrodynamic theories is used when both dissipation schemes attribute to the wetting process. This approach is, therefore, called the combined theory (Petrov and Petrov, 1992b). However, there is no complete and experimentally verified theory for the dynamic contact angle (Šikalo et al., 2005a). It has been shown (De Ruijter and De Coninck, 1997; De Ruijter et al., 1999; Seveno et al., 2010; Petrov and Petrov, 1992a; Hayes and Ralston, 1993; Schneemilch et al., 1998; Ranabothu et al., 2005; Blake and Clarke, 1997; De Ruijter et al., 1998; Blake, 2006; Bertrand et al., 2010) that the MKT model successfully describes the dynamic wetting behaviour in comparison with a wide range of experimental systems.

In this paper, the contact line velocity of a wetting phenomenon obtained using the transition state theory (TST) is related to that of the contact line velocity from the molecular kinetic approach. The relationship presented between the contact line velocity and the dynamic contact angle in a wetting process, introduces two microscopic parameters which are not known a priori. These two parameters, namely microscopic displacement frequency and length, are usually obtained using a curve-fitting of the measured data for the contact line velocity and dynamic contact angle and, therefore, are specific to a certain experiment for a specific substrate and liquid. In this study, a general correlation is developed for the microscopic displacement frequency that is only a function of the known values of a wetting process. This correlation is developed by improving the available correlation for the surface component of the specific activation free energy of wetting using a wide range of experimental data available in the literature. The predicted values from the correlation were in good agreement with those of the reported experiments even when a rough estimate value for the microscopic displacement length was used.

2 The wetting process from a TST point of view

The TST explains the reaction rates of elementary chemical reactions. The theory assumes a special type of chemical equilibrium (quasi-equilibrium) between reactants and activated transition state complexes. The Arrhenius relation as a TST equation, is derived from empirical observations (Anslyn and Dougherty, 2006) and gives the dependence of

the rate constant κ of chemical reactions on the temperature T and activation energy E_a , as (Blake and Haynes, 1969; Laidler and King, 1983; Pollak and Talkner, 2005):

$$\kappa = ae^{-E_a/RT} \tag{3}$$

where a is the attempt frequency of the reaction and R is the universal gas constant.

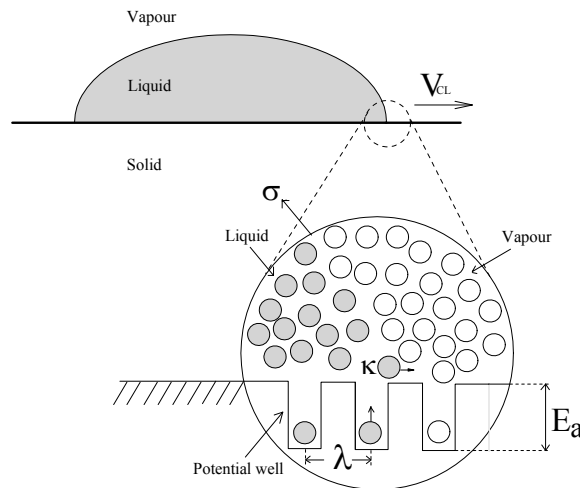
The contact of a liquid onto a solid can be considered an equilibrium state as long as the liquid molecules are confined within the solid potential well. The wetting/dewetting scenario occurs for the liquid molecules when they are positioned in the imbalance state. For example, for a liquid molecule to replace the adjacent gas molecule (wetting process), it should necessarily be driven from its own potential well to the adjacent well. This can only happen if the potential barrier of the molecule is distorted by a directed agent such as a shear stress. In fact, the spreading happens due to the initial imbalance at the contact line which results from the initial impulse transmitted to the liquid via the difference between the equilibrium and dynamic contact angles.

In the Arrhenius relation, when the activation energy is given in molecular units instead of molar units (e.g., joules per molecule instead of joules per mole) the Boltzmann constant (k_B) is used instead of the gas constant. Therefore, the Arrhenius relation for describing the transition state of a spreading process is:

$$\kappa = ae^{-E_a/k_B T} \tag{4}$$

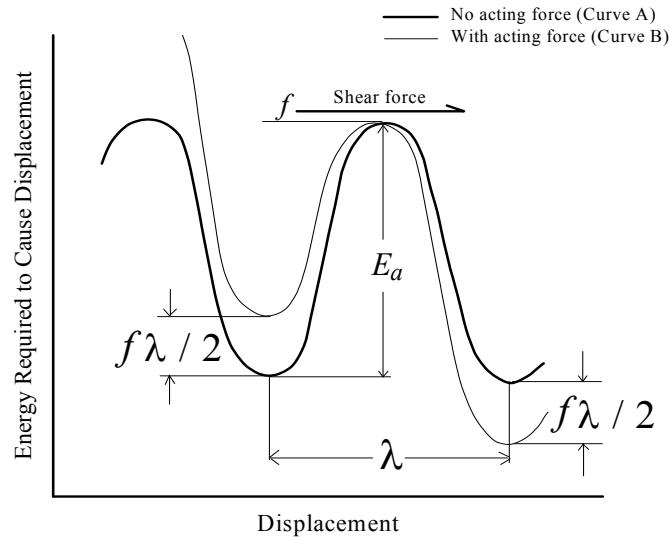
where a can be assumed to be equal to the attempt frequency of a molecule in the potential well (whether leading to the free state or not). Similarly, κ is the critical attempt frequency of a molecule in the potential well that results in the molecule to be positioned in the exit threshold from the barrier (the so-called free state of the molecule). It can be assumed that for a wetting/dewetting process, a liquid molecule moves in the horizontal direction on a solid surface by jumping from one potential well to the next over barriers of height E_a distance λ apart as displayed schematically in Figure 2.

Figure 2 A schematic representation of the wetting process and corresponding potential wells at a moving contact line



The basis of the above assumption is that the atoms and molecules participating in a wetting process are constrained from movement relative to each other by virtue of energy barriers separating adjacent equilibrium positions as depicted schematically in Figure 2 and curve A in Figure 3. The displacement of molecules to new positions requires that they become imbalanced by an external agent such as shear stress. In the absence of any applied force on the system, no molecular displacement is observed since the barriers will be crossed with equal attempt frequency in all directions. If, however, a directed agent such as a shear stress is applied to the system, the barriers heights become distorted as shown in Figure 3, curve B.

Figure 3 Representation of the potential wells in the state of equilibrium characterised by curve A and in the state of imbalance characterised by curve B



If f represents the force acting per molecule, then the barrier height is reduced by an amount $f\lambda / 2$ in the direction of the force and raised the same amount in the direction opposite to the force. The distance λ represents the distance between successive equilibrium positions; therefore, it may be called the microscopic displacement length. Since the barrier height in the direction of the force becomes $(E_a - f\lambda / 2)$ and in the direction opposite to the force $(E_a + f\lambda / 2)$, the net attempt frequency of molecular displacement in the direction of the force will be:

$$\begin{aligned}
 v_{net} &= \bar{v} - \bar{v} \\
 &= a \left[\exp\left(-\frac{E_a - f\lambda}{k_B T}\right) - \exp\left(-\frac{E_a + f\lambda}{k_B T}\right) \right] \\
 &= 2\kappa \sinh\left(\frac{f\lambda}{2k_B T}\right)
 \end{aligned} \tag{5}$$

where κ is known as the microscopic displacement frequency. Hence, the wetting-line velocity can be written as:

$$V_{CL} = v_{net} \lambda = 2\kappa\lambda \sinh\left(\frac{f\lambda}{2k_B T}\right) \quad (6)$$

The driving force for the contact line to move in a given direction when crossing one potential well is equal to the imbalance shear force that arises when equilibrium is disturbed; therefore, as a first approximation we may assume $f = \lambda\sigma(\cos\theta_e - \cos\theta_d)$. The resulting equation for the wetting-line velocity is then:

$$V_{CL} = 2\kappa\lambda \sinh\left[\frac{\sigma\lambda^2 (\cos\theta_e - \cos\theta_d)}{2k_B T}\right] \quad (7)$$

Blake and Haynes (1969) using the Eyring kind of approach (Gladstone et al., 1941) reached the same equation for the wetting-line velocity. The detailed development in this section, therefore, is an indication that the Arrhenius relation as a TST equation results in the same conclusion as of the Eyring approach.

3 Microscopic displacement frequency

The relationship obtained between the contact line velocity and dynamic contact angle, equation (7), introduces two unknown parameters namely κ and λ , the microscopic displacement frequency and length, respectively. The values reported from experimental data show a wide range of variation from 10^4 to 10^{12} Hz for κ . However, the reported values for λ are in the order of the molecular diameter (0.3 to 1.5 nm). Therefore, in this study the main focus is on improving the available correlation for κ by using Eyring's theory of absolute reaction rates along with available experimental data. The main advantage of the developed correlation is that it provides values of κ in terms of known physical properties of the liquid. As will be shown later in this paper, the developed correlation results in a good estimate of κ in comparison with those of the experiments. A typical experimental setup (De Ruijter and De Coninck, 1997) include a falling droplet from the tip of a needle immediately touching and spreading on a solid surface. The spreading of the droplets is captured by a CCD camera. For each velocity, the corresponding dynamic contact angle is measured directly from video images. Finally, a curve-fitting by equation (7) for V_{CL} versus θ_d gives measured values for the microscopic displacement frequency and length. The details of the experimental setup and procedure have been described in literature (De Ruijter and De Coninck, 1997; Phan et al., 2006; Bayer and Megaridis, 2006; Vega et al., 2007; Ray et al., 2008).

Blake and De Coninck (2002) approximated the microscopic displacement frequency in a wetting process as:

$$\kappa = \frac{\rho RT}{\mu M} \exp\left[\frac{-\Delta g_s}{k_B T} \lambda^2\right] \quad (8)$$

where M , ρ and μ are the molecular weight, density and dynamic viscosity of liquid, respectively, and Δg_s is the surface interaction component of the specific activation free energy of wetting. In order to obtain a relation between microscopic parameters and the known thermodynamic quantities, Blake and De Coninck (2002) approximated the specific activation free energy of the surface within the partial wetting domain (i.e., Δg_s)

as the reversible work of adhesion between the liquid and the solid surface (i.e., Wa). In other words, they assumed that:

$$\Delta g_s \approx Wa \quad (9)$$

where Wa is defined as (Adamson and Gast, 1997)

$$Wa = \sigma(1 + \cos\theta_e) \quad (10)$$

Therefore, as a first approximation it can be written:

$$\Delta g_s \approx \sigma(1 + \cos\theta_e) \quad (11)$$

Substituting for Δg_s from the above into equation (8), the microscopic displacement frequency can be obtained as (Blake, and De Coninck, 2002):

$$\kappa = \frac{\rho RT}{\mu M} \exp\left[\frac{-\sigma(1 + \cos\theta_e)}{k_B T} \lambda^2\right] \quad (12)$$

To inspect the accuracy of this relation, we performed a comparison between the calculated values based on equation (12) with those of the reported experiments. It was found that the values obtained from equation (12) underestimates those of the experiments for nearly all cases considered (except for water on PET and on Nylon). A more discussion of this comparison and the experimental cases will be discussed later in this section. Therefore, in this study, we propose to modify the approximate relation for the specific activation free energy [equation (11)] by subtracting a value based on the following relation:

$$\Delta g_s = Wa - \sigma_0(\mu, \sigma, \rho, M, \theta_e) \quad (13)$$

where a parameter σ_0 is proposed which, in general, can be a function of dynamic viscosity, surface tension, liquid density, liquid molecular weight and equilibrium contact angle. Performing a dimensional analysis for this parameter results into two dimensionless values of σ_0 / σ and $\mu^2 / \sigma(\rho^2 M)^{1/3}$, i.e.:

$$\frac{\sigma_0}{\sigma} = f\left(\frac{\mu^2}{\sigma(\rho^2 M)^{1/3}}, \theta_e\right) \quad (14)$$

To obtain a correlation for the dimensionless parameter (σ_0 / σ), reported values of various experiments in the literature were used as follows. Substituting for Δg_s from equation (13) into equation (8), we may obtain:

$$\kappa = \frac{\rho RT}{\mu M} \exp\left[\frac{\sigma_0(\mu, \sigma, \rho, M, \theta_e) - Wa}{k_B T} \lambda^2\right] \quad (15)$$

The functionality of σ_0 with respect to its proposed variables [equation (14)] can be determined using a curve-fitting of various reported experimental values. The experiments employed for this purpose and their corresponding values of κ and λ are given in Table 1.

Table 1 Microscopic wetting parameters (κ , λ) and physical properties of various liquid/solid systems from experiments (the reference of each case is given in the last column)

Liquid	Solid	$\rho(\text{kg/m}^3)$	$\mu(\text{pa}\cdot\text{s})$	$\sigma(\text{mN/m})$	$\Theta_c(0)$	$D(\text{nm})$	$\kappa(\text{s}^{-1})$	$\lambda(\text{nm})$	Ref.
Methylene iodide	Nylon	3,325	5×10^{-4}	51	41	0.51	1.4×10^7	0.8	Ray et al. (2008)
65.5% thiodiglycol/water	Nylon	1,134	0.0108	52.2	17.6	0.50	5.5×10^5	0.795	Vega et al. (2007)
Hexadecane	Nylon	770	0.0027	27	60.5	0.78	4×10^6	1.3	Bayer and Megaridis (2006)
Benzyl alcohol	Nylon	1,042	0.0058	39	56	0.55	9.9×10^8	1.0	Bayer and Megaridis (2006)
Water	Nylon	1,000	0.001	72.8	44.4	0.31	1.6×10^7	0.505	Vega et al. (2007)
Ethyl alcohol	Nylon	785	0.00107	22	63.2	0.46	5.4×10^7	1.7	Bayer and Megaridis (2006)
60% glycerol/water	Nylon	1,152	0.0096	65.8	59.4	0.37	4.3×10^5	0.805	Vega et al. (2007)
PDMS	Nylon	937	0.0096	19.6	9.7	1.0	3×10^7	0.792	Vega et al. (2007)
Squalane	Nylon	810	0.035	31.1	34.5	0.95	2.3×10^6	0.893	Vega et al. (2007)
16% glycerol/water	PET	1,036	0.0015	69.7	72.5	0.32	3.6×10^9	0.46	Blake (2006)
86% glycerol/water	PET	1,224	0.104	65.8	65	0.43	3.5×10^7	0.46	Blake (2006)
Water	PET	1,000	0.001	72.4	82	0.31	8.6×10^9	0.36	Blake (2006)
Di-n-butyl phthalate	PET	1,043	0.0196	34.3	5.4	0.76	1.1×10^5	1.77	Blake (2006)
Squalane	PET	811	0.029	30.7	15	0.95	6.3×10^5	1.09	De Ruijter and De Coninck (1997)
Octane	Teflon	703	5.4×10^{-4}	21.8	26	0.64	2.8×10^8	0.98	Bayer and Megaridis (2006)
Dioctyl sebacate	Teflon	915	0.025	31.2	61	0.91	2×10^4	1.4	Bayer and Megaridis (2006)
Hexadecane	Steel	773	0.0033	27.8	4	0.78	9×10^6	1.2	Bayer and Megaridis (2006)
Ethanol	Steel	790	0.0012	22.8	5	0.46	1.0×10^8	1.0	Bayer and Megaridis (2006)
Squalane	Glass	809	0.029	30.7	17.4	0.95	9.6×10^5	1.1	De Ruijter and De Coninck (1997)
Ethylene glycol	Glass	1,109	0.0218	48.2	33.5	0.45	1.9×10^3	1.47	Ranabothu et al. (2005)
Formamide	Glass	1,113	0.0032	58.2	30.5	0.40	5.5×10^4	1.07	Ranabothu et al. (2005)
Water (HPLC)	Glass	998	0.000995	72.8	54.1	0.31	1.19×10^4	1.02	Ranabothu et al. (2005)
Hexadecane	AF 1600	774	0.0033	26.9	69	0.78	5×10^6	1.4	Schneemilch et al. (1998)
Ethanol	si(111)	789	0.0017	22.8	25	0.46	2.0×10^9	1.3	Ray et al. (2008)
Hexane	si(111)	678	0.0012	18.4	38	0.60	1×10^{10}	1.4	Ray et al. (2008)

Table 2 A comparison between the values of κ predicted from equation (19) with those of the Blake and De Coninck (2002) correlation [equation (12)] and those of the reported experiments (references as in Table 1)

<i>Liquid</i>	<i>Solid</i>	$\kappa(s^{-1})^a$	$\kappa(s^{-1})^b$	$\kappa(s^{-1})^c$
Methylene iodide	Nylon	1.4×10^7	2.4×10^8	6×10^4
65.5% thiodiglycol/water	Nylon	5.5×10^5	8.6×10^6	5.2×10^2
Hexadecane	Nylon	4×10^6	5.2×10^6	2.2×10^2
Benzyl alcohol	Nylon	9.95×10^8	1.5×10^7	1.7×10^3
Water	Nylon	1.659×10^7	6.5×10^9	6.3×10^7
Ethyl alcohol	Nylon	5.4×10^7	6.1×10^6	8.3
60% glycerol/water	Nylon	4.3×10^5	2.7×10^7	1.5×10^3
PDMS	Nylon	3.1×10^7	3.8×10^7	9.5×10^5
Squalane	Nylon	2.3×10^6	4.9×10^6	2.4×10^3
16% glycerol/water	PET	3.6×10^9	1.3×10^{10}	8.1×10^8
86% glycerol/water	PET	3.5×10^7	3.2×10^8	4.2×10^6
Water	PET	8.6×10^9	5×10^{10}	1.0×10^{10}
Di-n-butyl phthalate	PET	1.1×10^5	5.3	1.5×10^{-14}
Squalane	PET	6.3×10^5	5.9×10^5	4.9
Octane	Teflon	2.84×10^8	6.2×10^8	1.9×10^6
Diocetyl sebacate	Teflon	2×10^4	2×10^5	6.3×10^{-2}
Hexadecane	Steel	9×10^6	1.3×10^6	10.6
Ethanol	Steel	1.0×10^8	4.6×10^8	6×10^5
Squalane	Glass	9.6×10^5	5.5×10^5	4
Ethylene glycol	Glass	1.97×10^3	3.1×10^2	1.8×10^{-11}
Formamide	Glass	5.534×10^4	1.5×10^5	1.8×10^{-3}
Water (HPLC)	Glass	1.19×10^4	1.4×10^6	3.4×10^{-2}
Hexadecane	AF 1600	5×10^6	3.3×10^6	78.7
Ethanol	si(111)	2×10^9	3.6×10^7	7.8×10^2
Hexane	si(111)	1.0×10^{10}	1.1×10^8	9.9×10^3

Notes: ^aexperimental values available in the literature^bpredicted values by equation (19)^cpredicted values by the Blake and De Coninck (2002) correlation [equation (12)].

Having experimental data of this table and using equation (15), the corresponding values of σ_0 is first obtained. A curve-fitting of the resulting data for σ_0 / σ against the dimensionless parameters of equation (14) results in the following correlation for σ_0 / σ :

$$\frac{\sigma_0}{\sigma} = 0.00078 \frac{\mu}{\sqrt{\rho\sigma D}} + 0.6(1 + \cos\theta_e) \quad (16)$$

where D is the molecular diameter of the liquid defined as $D = (M / \rho N_a)^{1/3}$ where N_a is the Avogadro number. To evaluate the improved accuracy of the modified equation, we assume that the average error in the fit is given by:

$$Error = \frac{\sum_{n=1}^N |\sigma_0^f - \sigma_0^m| / \sigma_0^m}{N} \times 100 \quad (17)$$

where N is the number of experimental points, σ_0^f is the fitted value predicted by equation (16) and σ_0^m is the measured value obtained from equation (15). The average error between the developed correlation [equation (16)] and the experimental values is nearly 27% excluding the two cases of water on PET and Nylon in Table 2 (as above-mentioned σ_0^m for these two cases become negative).

Combining equations (15) and (16), we obtain:

$$\kappa = \frac{\rho RT}{\mu M} \exp \left(\frac{0.00078\sigma \frac{\mu}{\sqrt{\rho\sigma D}} + 0.6\sigma(1 + \cos\theta_e) - Wa}{k_B T} \lambda^2 \right) \quad (18)$$

or

$$\kappa = \frac{\rho RT}{\mu M} \exp \left(\frac{0.00078\mu \sqrt{\frac{\sigma}{\rho D}} - 0.4Wa}{k_B T} \lambda^2 \right) \quad (19)$$

To assess the accuracy of this correlation, the values of κ predicted from equation (19) will be compared to those of the experiments and Blake and De Coninck (2002) correlation [equation (12)] in the next section.

4 Discussion

In this paper, it was shown that the Arrhenius relation may be used as a powerful tool for the description and prediction of the transition process of a wetting/dewetting phenomenon. This relation, therefore, was used to model the wetting-line velocity of a liquid spreading scenario which led to equation (7). The equation, however, included an important microscopic parameter (κ) for which we developed a correlation [equation (19)]. A detailed discussion of this correlation is presented in this section.

4.1 Theoretical examination of the developed correlation

As mentioned before, when developing equation (19), the solid/liquid interactions are main sources of energy dissipation within the moving three-phase zone. Therefore, for weak solid/liquid interactions, equation (7) predicts θ_d as a weak function of V_{CL} , and vice versa. Substituting for σ_0 from equation (16) into equation (13) and using the definition of the molecular volume as $v_l = M / \rho N_a$, the surface interaction component (Δg_s) may be obtained as:

$$\Delta g_s = 0.4Wa - 0.00078\mu \sqrt{\frac{\sigma}{\rho}} (v_l)^{-1/6} \quad (20)$$

where the molecular diameter D in equation (16) has been replaced by molecular volume (v_l) using $D = (v_l)^{1/3}$.

If the argument of the sinh function in equation (7) is small, e.g., when dealing with contact angles close to θ_e , as a first order approximation, equation (7) reduces to the linear form:

$$V_{CL} = \frac{\sigma(\cos\theta_e - \cos\theta_d)}{\zeta} \quad (21)$$

where

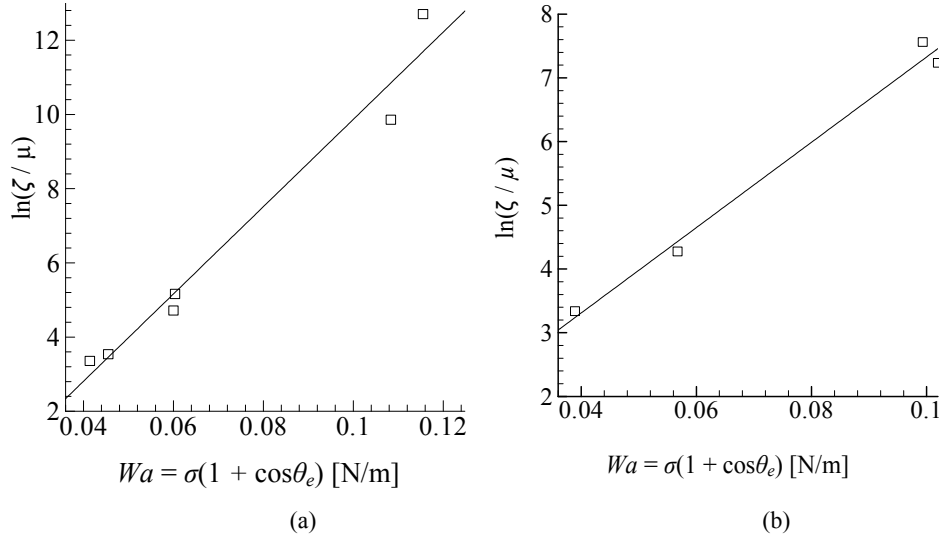
$$\zeta = \frac{k_B T}{\kappa \lambda^3} \quad (22)$$

ζ is the coefficient of contact-line friction (De Ruijter et al., 1999) and has the physical dimension of the shear viscosity. It describes the friction of the liquid molecules on the solid substrate per unit length of the contact line. It has been shown that ζ gives a useful description of dissipation within the three-phase zone and can be compared with the dynamic viscosity (Blake, 2006; Blake and De Coninck, 2002). Substituting for Δg_s from equation (20) into equation (8), the contact-line friction from equation (22) can be written as:

$$\zeta = \frac{\mu v_l}{\lambda^3} \exp \left[\frac{\lambda^2}{k_B T} \left(0.4Wa - 0.00078\mu \sqrt{\frac{\sigma}{\rho}} (v_l)^{-1/6} \right) \right] \quad (23)$$

This relation predicts that ζ (contact-line friction) increases with Wa (the work of adhesion); i.e., assuming λ to be constant, $\ln(\zeta / \mu)$ varies linearly versus Wa with a positive slope of $0.4\lambda^2 / k_B T$. To check the accuracy of this relation, we have plotted $\ln(\zeta / \mu)$ versus Wa for two groups of various liquid/solid experiments (from Table 1) where the assumption of constant λ is nearly valid for each group. The experiments selected for the first group (group A) are: Squalane on PET, Octane on Teflon, Ethanol on Steel, Formamide on Glass, Squalane on Glass and water on Glass; where λ varies from 0.98 to 1.1 (with a mean value of 1.043). For the second group (group B), λ ranges from 0.792 to 0.893 (with a mean value of 0.821); the experiments in this group include: 60% w/w glycerol/water mixture, 65.5% w/w thiodiglycol/water mixture, tri methyl poly dimethyl siloxane (PDMS) and squalane on nylon monofilament substrate. Figure 4(a) and Figure 4(b) display the variation of $\ln(\zeta / \mu)$ versus Wa for the group A and group B of experiments, respectively, where the value of ζ is obtained using equation (22) based on experimental values of κ and λ . Linear regression of these plots give straight lines with a slope of 117.6 for group A experiments and a slope of 55.4 for those of group B. The quality-of-fit parameter ($= R^2$) was 0.967 and 0.932 for group A and B, respectively. The slope of variation of $\ln(\zeta / \mu)$ versus Wa based on equation (23) is $0.4\lambda^2 / k_B T$. Using a value of $T = 300$ K, the two slope values of 117.6 and 66.94 results in a value of λ equal to 1.103 for group A experiments and 0.832 for group B which are close to those of the experiments: 1.043 for group A and 0.821 for group B. This comparison verifies that the functional dependency of κ with respect to Wa based on the developed correlation [equation (19)] is acceptable.

Figure 4 Variation of $\ln(\zeta / \mu)$, the logarithm values of contact-line friction coefficient made dimensionless by the liquid viscosity, versus the work of adhesion Wa for, (a) group A (b) group B experiments (detailed in the text)



Notes: A linear regression of the two plots with a straight line results in
 $y = 117.6 \times -1.893$ (with a quality-of-fit value $R^2 = 0.967$) for group A and
 $y = 66.94 \times +0.633$ (with $R^2 = 0.987$) for group B.

4.2 Experimental examination of the developed correlation

The accuracy of predictions from equation (19) is examined by a comparison with experimental data for various liquid/surface combinations. The values of κ obtained from this relation are compared with those of the Blake and De Coninck (2002) correlation [equation (12)] and those of the various experiments in Table 2. The agreement between κ values from equation (19) and experiments for nearly 36% of the cases is in the same order.

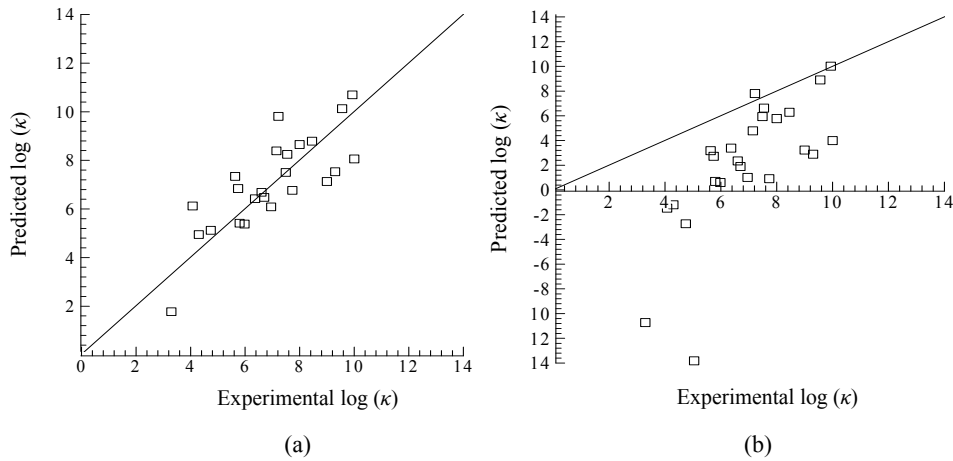
The discrepancy between the two results may be attributed to the assumption of a simple liquid [as mentioned in equation (11)] in the derivation of equation (19). When the reported value of λ is much larger than the liquid molecular diameter, the discrepancy between the predicted values and experiments was increased. For 40% of the cases, the discrepancy is in one order of magnitude difference and for 24% of the cases is more than one order of magnitude.

However, it can be seen that for nearly 90% of the cases, the predicted values using the developed correlation in this paper are in a better agreement with experiments compared to those of the Blake and De Coninck correlation.

A better presentation of equation (19) in comparison with the experiments can be displayed in a logarithmic plot as seen in Figure 5. To show the accuracy of the presented correlation compared to that of the Blake and De Coninck correlation [equation (12)], the predicted values from equations (19) and (12) are plotted against the same experimental values in Figure 5(a) and Figure 5(b), respectively. As the figure shows, an ideal prediction of the measurements would fall along the 45° line. Predictions from equation (12) tend to lie under the 45° line [see Figure 5(b)] indicating that the Blake and

De Coninck correlation underestimates the microscopic displacement frequency. The values obtained using the presented correlation in this study [equation (19)], however, cluster around the 45° line meaning that the predictions of equation (19) are closer to the experimental values. It can be concluded, therefore, that the proposed correlation [equation (19)] better predicts the values of κ compared to that of equation (12) for a wide range of wetting scenarios with various liquids and solids. It is clear that a better estimation of the microscopic displacement frequency leads to a more accurate prediction of the contact line velocity based on equation (7). It should be mentioned that the main advantage of equation (19) is that it only correlates the known values of the liquid in a wetting process.

Figure 5 A logarithmic plot of the experimental values (given in Table 1) for the microscopic displacement frequency in comparison with the predicted values using, (a) developed correlation by equation (19) (b) the Blake and De Coninck (2002) correlation [equation (12)]



As observed from the above discussion, the predicted values of κ are highly sensitive to the values of the molecular displacement length λ . The parameter λ is influenced by the size of the liquid molecules and is somewhat larger than the molecular diameter (Bayer and Megaridis, 2006; Schneemilch et al., 2000; Blake and De Coninck, 2004; Ray et al., 2008). It is possible to provide an estimate value of displacement λ based on the definition of the molecular volume as follows. As shown schematically in Figure 2, as a first approximation we assume this distance to be proportional to the size of the molecule as:

$$\lambda \approx C(v_l)^{1/3} \quad (24)$$

where v_l is the molecular volume and C is a constant. To evaluate the constant C , we performed a curve-fitting of the experimental values of λ (given in Table 1) which lead to $C = 1.6$. To investigate the accuracy of equation (24) with $C = 1.6$, the values of λ obtained from this relation and those of the various experiments for the parameter λ are compared in Table 3. The estimated λ from equation (24) shows a good agreement with the experimental values for nearly most of the cases (the average error for 80% of the cases is around 21%).

Table 3 A comparison between λ values predicted from equation (24) and those of the experiments for various solid/liquid systems (references as in Table 1)

<i>Liquid</i>	<i>Solid</i>	λ (nm) ^a	λ (nm) ^b	<i>Error (%)</i>
Methylene iodide	Nylon	0.800	0.818	2.3
65.5% thiodiglycol/water	Nylon	0.795	0.803	1
Hexadecane	Nylon	1.3	1.259	3.1
Benzyl alcohol	Nylon	1.0	0.890	11
Water	Nylon	0.505	0.497	1.6
Ethyl alcohol	Nylon	1.7	0.736	56
60% glycerol/water	Nylon	0.805	0.590	26
PDMS	Nylon	0.792	1.775	124
Squalane	Nylon	0.893	1.526	70
16% glycerol/water	PET	0.46	0.513	11
86% glycerol/water	PET	0.46	0.687	49
Water	PET	0.36	0.497	37
Di-n-butyl phthalate	PET	1.77	1.219	31
Squalane	PET	1.09	1.525	39
Octane	Teflon	0.98	1.033	5.4
Dioctyl sebacate	Teflon	1.4	1.468	4.8
Hexadecane	Steel	1.2	1.258	4.7
Ethanol	Steel	1.0	0.736	26
Squalane	Glass	1.1	1.525	38
Ethylene glycol	Glass	1.47	0.724	50
Formamide	Glass	1.07	0.650	39
Water (HPLC)	Glass	1.02	0.497	51
Hexadecane	AF 1600	1.4	1.258	10
Ethanol	si(111)	1.3	0.736	43
Hexane	si(111)	1.4	0.963	31

Notes: ^aexperimental values available in the literature
^bestimated values from equation (24).

To further elaborate the good approximation of equation (24), the estimated values for the parameter λ from this equation are substituted into equation (19) and the resulting values of κ are compared with those of the experiments in Table 4. As observed, the developed correlation in this paper [equation (19)] leads to good estimate values for κ even when a rough estimate value for λ is used. Equation (24) does not consider the solid surface properties. The nature of the solid surface is thought to influence the parameter λ (Ray et al., 2008) that is related to the available surface sites for molecular adsorption. It seems, therefore, that considering substrate properties such as roughness and/or equilibrium contact angle in equation (24) may result to a more accurate relation for λ . Developing such a relation, however, needs further theoretical and experimental studies.

Table 4 A comparison between κ values predicted using equation (19) based on estimate values for λ from equation (24) with those of the reported experiments (references as in Table 1)

<i>Liquid</i>	<i>Solid</i>	$\kappa(s^{-1})^a$	$\kappa(s^{-1})^b$
Methylene iodide	Nylon	1.4×10^7	1.9×10^8
65.5% thiodiglycol/water	Nylon	5.5×10^5	7.8×10^6
Hexadecane	Nylon	4×10^6	7.7×10^6
Benzyl alcohol	Nylon	9.95×10^8	4.9×10^7
Water	Nylon	1.659×10^7	7.2×10^9
Ethyl alcohol	Nylon	5.4×10^7	7.7×10^9
60% glycerol/water	Nylon	4.3×10^5	3.9×10^8
PDMS	Nylon	3.1×10^7	1.1×10^4
Squalane	Nylon	2.3×10^6	8.6×10^3
16% glycerol/water	PET	3.6×10^9	8.6×10^9
86% glycerol/water	PET	3.5×10^7	1.9×10^8
Water	PET	8.6×10^9	2×10^{10}
Di-n-butyl phthalate	PET	1.1×10^5	8×10^4
Squalane	PET	6.3×10^5	2.7×10^3
Octane	Teflon	2.84×10^8	4.1×10^8
Dioctyl sebacate	Teflon	2×10^4	9.8×10^4
Hexadecane	Steel	9×10^6	6.6×10^5
Ethanol	Steel	1.0×10^8	3.4×10^9
Squalane	Glass	9.6×10^5	2.9×10^3
Ethylene glycol	Glass	1.97×10^3	4.5×10^7
Formamide	Glass	5.534×10^4	5.5×10^8
Water (HPLC)	Glass	1.19×10^4	9×10^9
Hexadecane	AF 1600	5×10^6	1.2×10^7
Ethanol	si(111)	2×10^9	4.2×10^9
Hexane	si(111)	1.0×10^{10}	3×10^9

Notes: ^aExperimental values available in the literature.^bPredicted values by substituting estimate value for λ from equation (24) into equation (19).

5 Conclusions

In this paper, a correlation was developed for the microscopic displacement frequency in a wetting phenomenon that is only a function of the known values of the process. The presented expression in conjunction with the Arrhenius equation can be used to predict the dynamic contact angle as a function of the contact line velocity. The correlation was obtained by improving the available relation for the surface component of the specific activation free energy of a wetting process using a curve-fitting of a wide range of experimental data. A theoretical examination of the developed correlation verified its

validity for various wetting scenarios. The predicted values from the correlation were in good agreement with those of the reported experiments even when a rough estimate value for the microscopic displacement length was used. The correlations introduced in this study, can be used to predict the contact-line friction as well as the dynamic contact angle in terms of the known values of a wetting process. The detail developments in this study provide a more insight towards the microscopic parameters that influence a dynamic wetting.

References

- Adamson, A.W. and Gast, A.P. (1997) *Physical Chemistry of Surfaces*, 6th ed., Wiley, New York.
- Anslyn, E.V. and Dougherty, D.A. (2006) 'Transition state theory and related topics', *Modern Physical Organic Chemistry*, pp.365–373, University Science Books, Sausalito.
- Bayer, I. and Megaridis, C.M. (2006) 'Contact angle dynamics in droplets impacting on flat surfaces with different wetting characteristic', *J. Fluid Mech.*, Vol. 558, pp.415–449.
- Bayer, I.S. (2006) *Measurement and Interpretation of Contact Angles in Surface Energetic and Droplet Impact*, PhD thesis, University of Illinois at Chicago.
- Bertrand, E., Blake, T.D. and De Coninck, J. (2010) 'Dynamics of dewetting', *Colloids Surfaces A*, Vol. 369, Nos. 1–3, pp.141–147.
- Blake, T.D. (2006) 'The physics of moving wetting lines', *J. Colloid Interface Sci.*, Vol. 299, No. 1, pp.1–13.
- Blake, T.D. and Clarke, A. (1997) 'Contact angle relaxation during droplet spreading: comparison between molecular kinetic theory and molecular dynamics', *Langmuir*, Vol. 13, No. 7, pp.2164–2166.
- Blake, T.D. and De Coninck, J. (2002) 'The influence of solid-liquid interactions on dynamic wetting', *Adv. Colloid Interface Sci.*, Vol. 96, Nos. 1–3, pp.21–36.
- Blake, T.D. and De Coninck, J. (2004) 'The influence of pore wettability on the dynamics of imbibition and drainage', *Colloids Surf. A*, Vol. 250, Nos. 1–3, pp.395–402.
- Blake, T.D. and Haynes, J.M. (1969) 'Kinetic of liquid/liquid displacement', *J. Colloid Interface Sci.*, Vol. 30, No. 3, pp.421–423.
- Blake, T.D. and Shikhmurzaev, Y.D. (2002) 'Dynamic wetting by liquids of different viscosity', *J. Colloid Interface Sci.*, Vol. 253, No. 1, pp.196–202.
- Blake, T.D., Bracke, M. and Shikhmurzaev, Y.D. (1999) 'Experimental evidence of nonlocal hydrodynamic influence on the dynamic contact angle', *Phys. Fluids*, Vol. 11, No. 8, pp.1995–2007.
- Blake, T.D., De Coninck, J. and D'Ortona, U. (1995) 'Models of wetting: Immiscible lattice Boltzmann automata versus molecular kinetic theory', *Langmuir*, Vol. 11, No. 11, pp.4588–4592.
- Bonn, D., Eggers, J., Indekeu, J., Meunier, J. and Rolley, E. (2009) 'Wetting and spreading', *Rev. Mod. Phys.*, Vol. 81, No. 2, pp.739–805.
- Brochard-Wyart, F., Herve, H., Redon, C. and Rondelez, F. (1991) 'Spreading of heavy droplets', *J. Colloid Interface Sci.*, Vol. 142, No. 2, pp.518–527.
- Bussmann, M., Mostaghimi, J. and Chandra, S. (1999) 'On a three-dimensional volume tracking model of droplet impact', *Phys. Fluids*, Vol. 11, No. 6, pp.1406–1417.
- Cherry, B.W. and Holmes, C.M. (1969) 'Letters to the editors: kinetic of wetting of surfaces by polymer', *J. Colloid Interface Sci.*, Vol. 29, No. 1, pp.174–176.
- Chuang, Y., BangSheng, L., MingXing, R. and HengZhi, F. (2009) 'Kinetics of wetting of liquid on a solid surface', *Sci. China Ser. B-Chem.*, Vol. 52, No. 7, pp.868–873.

- Cox, R.G. (1986) 'The dynamics of the spreading of liquids on a solid surface. Part 1. Viscous flow', *J. Fluid Mech.*, Vol. 168, pp.169–194.
- De Gennes, P.G. (1985) 'Wetting: static and dynamic', *Rev. Mod. Phys.*, Vol. 57, No. 3, pp.827–863.
- De Ruijter, M., Kölsch, P., Voué, M., De Coninck, J. and Rabe, J.P. (1998) 'Effect of temperature on the dynamic contact angle', *Colloids Surf. A*, Vol. 144, Nos. 1–3, pp.235–243.
- De Ruijter, M.J. and De Coninck, J. (1997) 'Contact angle relaxation during the spreading of partially wetting drops', *Langmuir*, Vol. 13, No. 26, pp.7293–7298.
- De Ruijter, M.J., Blake, T.D. and De Coninck, J. (1999) 'Dynamic wetting studied by molecular modeling simulations of droplet spreading', *Langmuir*, Vol. 15, No. 22, pp.7836–7847.
- De Ruijter, M.J., Charlot, M., Voué, M. and De Coninck, J. (2000) 'Experimental evidence of several time scale in drop spreading', *Langmuir*, Vol. 16, No. 5, pp.2363–2368.
- Drelich, J., Zahn, R., Miller, J.D. and Borchardt, J.K. (2002) 'Contact angle relaxation for ethoxylated alcohol solutions on hydrophobic surfaces', in Mittal, K.L. (Ed.): *Proceedings of the 2nd International Symposium on "Contact Angles, Wettability and Adhesion"*, Newark, NJ, 21–23 June, VSP, Utrecht, The Netherlands, pp.253–264.
- Foister, R.T. (1990) 'The kinetics of displacement wetting in liquid/liquid/solid systems', *J. Colloid Interface Sci.*, Vol. 136, No. 1, pp.266–282.
- Fujimoto, H., Shiraishi, H. and Hatta, N. (2000) 'Evolution of liquid/solid contact area of a drop impinging on a solid surface', *Heat Mass Trans.*, Vol. 43, No. 9, pp.1673–1677.
- Fukai, J., Shiiba, Y., Yamamoto, T., Miyatake, O., Poulikakos, D., Megaridis, C.M. and Zhao, Z. (1995) 'Wetting effects on the spreading of a liquid droplet colliding with a flat surface: Experiment and modeling', *Phys. Fluids*, Vol. 7, No. 2, pp.236–247.
- Gladstone, S., Laidler, K.J. and Eyring, H.J. (1941) *The Theory of Rate Processes*, McGraw-Hill, New York.
- Hayes, R.A. and Ralston, J. (1993) 'Forced liquid movement on low energy surfaces', *J. Colloid Interface Sci.*, Vol. 159, No. 2, pp.429–438.
- Laidler, K.J. and Klng, M.C. (1983) 'The development of transition-state theory', *J. Phys. Chem.*, Vol. 87, No. 15, pp.2657–2664.
- Liang, Z.P., Wang, X.D., Duan, Y.Y., Min, Q., Wang, C. and Lee, D.J. (2010) 'Dynamic wetting of non-Newtonian fluids: multicomponent molecular-kinetic approach', *Langmuir*, Vol. 26, No. 18, pp.14594–14599.
- Lim, T., Han, S., Chung, J., Chung, J.T., Ko, S. and Grigoropoulos C.P. (2009) 'Experimental study on spreading and evaporation of inkjet printed pico-liter droplet on a heated substrate', *Heat Mass Transfer*, Vol. 52, Nos. 1–2, pp.431–441.
- Lopez, J. and Miller, C.A. (1976) 'Spreading kinetics of liquid drops on solids', *J. Colloid Interface Sci.*, Vol. 56, No. 3, pp.460–468.
- Pasandideh-Fard, M., Qiao, Y.M., Chandra, S. and Mostaghimi, J. (1996) 'Capillary effects during droplet impact on a solid surface', *Phys. Fluids*, Vol. 8, No. 3, pp.650–659.
- Petrov, J.G. and Petrov, P.G. (1992a) 'Forced advancement and retraction of polar liquids on a low energy surface', *Colloids Surf. A*, Vol. 64, No. 2, pp.143–149.
- Petrov, P.G. and Petrov, J.G., (1992b) 'A combined molecular-hydrodynamic approach to wetting kinetics', *Langmuir*, Vol. 8, No. 7, pp.1762–1767.
- Petrov, J.G., Ralston, J. and Hayes, R.A. (1999) 'Dewetting dynamics on heterogeneous surfaces: a molecular-kinetic treatment', *Langmuir*, Vol. 15, No. 9, pp.3365–3373.
- Petrov, J.G., Ralston, J., Schneemilch, M. and Hayes, R.A. (2003a) 'Dynamics of partial wetting and dewetting in well-defined systems', *J. Phys. Chem. B*, Vol. 107, No. 7, pp.1634–1645.
- Petrov, J.G., Ralston, J., Schneemilch, M. and Hayes, R.A. (2003b) 'Dynamics of partial wetting and dewetting of an amorphous fluoropolymer by pure liquids', *Langmuir*, Vol. 19, No. 7, pp.2795–2801.

- Phan, C.M., Nguyen, A.V and Evans, G.M. (2006) 'Combining hydrodynamics and molecular kinetics to predict dewetting between a small bubble and a solid surface', *J. Colloid Interface Sci.*, Vol. 296, No. 2, pp.669–676.
- Phan, C.M., Nguyen, A.V. and Evans, G.M. (2003) 'Assessment of hydrodynamic and molecular-kinetic models applied to the motion of the dewetting contact line between a small bubble and a solid surface', *Langmuir*, Vol. 19, No. 17, pp.6796–6801.
- Pollak, E. and Talkner, P. (2005) 'Reaction rate theory: what it was, where is it today, and where is it going?', *Chaos: An Interdisciplinary Journal of Nonlinear Science*, Vol. 15, No. 2, p.026116(1–11).
- Ranabothu, S.R., Karnezis, C. and Dai, L.L. (2005) 'Dynamic wetting: hydrodynamic or molecular-kinetic?', *J. Colloid Interface Sci.*, Vol. 288, No. 1, pp.213–221.
- Ray, S., Sedev, R., Priest, C. and Ralston, J. (2008) 'Influence of the work of adhesion on the dynamic wetting of chemically heterogeneous surfaces', *Langmuir*, Vol. 24, No. 22, pp.13007–13012.
- Roisman, I.V., Opfer, L., Tropea, C., Raessi, M., Mostaghimi, J. and Chandra, S. (2008) 'Drop impact onto a dry surface: role of the dynamic contact angle', *Colloids Surf. A*, Vol. 322, Nos. 1–3, pp.183–191.
- Roux, D.C.D. and Cooper-White, J.J. (2004) 'Dynamics of water spreading on a glass surface', *J. Colloid Interface Sci.*, Vol. 277, No. 2, pp.424–436.
- Schneemilch, M., Hayes, R.A., Petrov, J.G. and Ralston, J. (1998) 'Dynamic wetting and dewetting of a low-energy surface by pure liquids', *Langmuir*, Vol. 14, No. 24, pp.7047–7051.
- Schneemilch, M., Welters, W.J.J., Hayes, R.A. and Ralston, J. (2000) 'Electrically induced changes in dynamic wettability', *Langmuir*, Vol. 16, No. 6, pp.2924–2927.
- Seveno, D., Dinter, N. and De Coninck, J. (2010) 'Wetting dynamics of drop spreading: new evidence for the microscopic validity of the molecular-kinetic theory', *Langmuir*, Vol. 26, No. 18, pp.14642–14647.
- Shikhmurzaev, Y.D. (1993) 'The moving contact line on a smooth solid surface', *Int. J. Multiphase Flow*, Vol. 19, No. 4, pp.589–610.
- Šikalo, S., Tropea, C. and Ganic, E.N. (2005a) 'Dynamic wetting angle of a spreading droplet', *Exp. Thermal Fluid Sci.*, Vol. 29, No. 7, pp.795–802.
- Šikalo, S., Wilhelm, H.D., Roisman, I.V., Jakirlic, S. and Tropea, C. (2005b) 'Dynamic contact angle of spreading droplets: experiments and simulations', *Phys. Fluids*, Vol. 17, Nos. 6, p.062103(1–13).
- Vega, M.J., Gouttiere, C., Seveno, D., Blake, T.D., Voué, M. and De Coninck, J. (2007) 'Experimental investigation of the link between static and dynamic wetting by forced wetting of nylon filament', *Langmuir*, Vol. 23, No. 21, pp.10628–10634.
- Wang, M.J., Hung, Y.L., Lin, F.H. and Lin, S.Y. (2009) 'Dynamic behaviors of droplet impact and spreading: a universal relationship study of dimensionless wetting diameter and droplet height', *Exp. Thermal Fluid Sci.*, Vol. 33, No. 7, pp.1112–1118.
- Wang, M.J., Lin, F.H., Ong, Y.J. and Lin, S.Y. (2009) 'Dynamic behaviors of droplet impact and spreading-water on glass and paraffin', *Colloids Surf. A*, Vol. 339, Nos. 1–3, pp.224–231.
- Werner, S.R.L., Jones, J.R., Paterson, A.H.J., Archer, R.H. and Pearce, D.L. (2007) 'Droplet impact and spreading: droplet formulation effects', *Chem. Eng. Sci.*, Vol. 62, No. 9, pp.2336–2345.
- Xiaodong, W., Xiaofeng, P. and Duzhong, L. (2003) 'Dynamic wetting and stress singularity on contact line', *Sci. China Ser. E*, Vol. 46, No. 4, pp.407–417.
- Xiaodong, W., Xiaofeng, P., Yuanyuan, D. and Buxuan, W. (2007) 'Dynamics of spreading of liquid on solid surface', *China J. Chem. Eng.*, Vol. 15, No. 5, pp.730–737.

Nomenclature

a	The attempt frequency of a molecule in the potential well
D	Molecular diameter of liquid ($= (v_l)^{1/3}$)
f	Imbalance force per unit length of the wetting line ($= \sigma(\cos\theta_e - \cos\theta_d)$)
G	The molar activation free energy
Δg	The specific activation free energy of wetting
h	Planck's constant ($= 6.626 \times 10^{-34} \text{J.s}$)
k_B	Boltzmann's constant ($= 1.381 \times 10^{-23} \text{J.K}^{-1}$)
M	Molecular weight
N	Avogadro's number ($= 6.023 \times 10^{23} \text{mol}^{-1}$)
n	The number of adsorption sites per unit area
R	Gas constant ($= 8.314 \text{J.K}^{-1} \text{mol}^{-1}$)
S	Spreading coefficient
T	Temperature
V_{CL}	Contact line velocity
v_l	Molecular volume ($= M / \rho N_a$)
Wa	The reversible work of adhesion ($= \sigma(1 + \cos\theta_e)$)

Greek symbols

θ_d	Dynamic contact angle
θ_e	Equilibrium contact angle
κ	Microscopic displacement frequency (s^{-1})
λ	Distance of potential well to the next
μ	Dynamic viscosity
ρ	Density
σ	Surface tension

Subscripts

a	Activation
B	Boltzmann
d	Dynamic
e	Equilibrium
l	Liquid
s	Solid
v	Vapour/viscous
