Influence of solid-liquid interactions on dynamic wetting: evidence from molecular dynamics and experiment

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Objective

All liquid printing or coating methods depend on effective and efficient wetting and/or dewetting, i.e. both statics and dynamics are important. Wetting dynamics are equally important for the spreading or movement of drops on surfaces.

Strong solid-liquid interactions favor wetting and adhesion.

But how do they effect wetting dynamics, and are they always desirable?
There are many processes in which contact angles are important:

- Detergency/Weatherproofing
- Textiles/Dyeing
- Mineral flotation
- Plant protection
- Powder dispersion
- Dust control
- Coating
- Oil recovery
- Road making
- Distillation
- Temperature
- Casting
- Soldering
- Inks and adhesives
- Groundwater flow
- Biosystems

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Approach

• Use large-scale molecular dynamics (MD) to model wetting
• Study influence of solid-liquid (S-L) interactions over wide range
• Interpret the results
• Infer practical consequences
Dynamics of wetting?
It is known that $\theta_t$ is a function of the speed $\frac{dx}{dt}$.

\[
\frac{dx}{dt} = f(\cos \theta_0 - \cos \theta_t)
\]

The out-of-balance interfacial tension forces can be compensated by three channels of dissipation (de Gennes):

- **viscous dissipation in the bulk of the liquid**;
- **dissipation in the close vicinity of the solid near the wetting line**;
- **dissipation in the precursor film, associated with the complete wetting**;
In its most simple form, the equation describing the change in the dynamic contact angle due to viscous bending may be written in terms of the capillary number as

\[
\theta_D^3 - \theta_m^3 = 9Ca \ln \left( \frac{L}{L_m} \right), \quad \theta < \frac{3\pi}{4}
\]

where
- \( \mu \) = dynamic viscosity
- \( \gamma \) = surface tension of the liquid
- \( L \) = macroscopic length scales, \( L = 10 \text{ mm} \)
- \( L_m \) = microscopic length scale \( \sim 1 \text{ nm} \)

leading to \( \ln() \sim 10 \).

The hydrodynamic model

Motion for a viscous fluid: N-S

Neglecting inertia, steady motion, no external force:

\[
\rho \frac{\partial \vec{v}}{\partial t} + \rho \left( \vec{v} \cdot \text{grad} \right) \vec{v} = \rho \vec{f} - \left( \text{grad} \right) p + \eta \Delta \vec{v}
\]

\[
\left( \text{grad} \right) p = \eta \Delta \vec{v}
\]

Voinov, 1976
Molecular-kinetic theory

- Molecular model with energy barriers to molecular displacement
- Maxwell-Boltzmann statistics
- Surface tension driving force $f_W$ due to disturbed equilibrium

$$U_{CL} = 2\kappa_0^W \lambda \sinh \left[ \frac{\gamma_{LV}}{2nk_BT} \left( \cos \theta^0 - \cos \theta \right) \right]$$

$$\kappa_0^W = k_BT / h \exp \left( \frac{-\Delta g^*_w}{nk_BT} \right)$$

Near $\theta^0$, $U_{CL} = \left( \frac{\kappa^0 \lambda^3}{k_BT} \right) \gamma_{LV} \left( \cos \theta^0 - \cos \theta \right)$

hence, $U_{CL} = f_W / \xi_0^W$  $\xi_0^W$ = coefficient of contact-line friction

Equations usually tested by fitting experimental data to give $\kappa^0$ and $\lambda$
Data in linear region give $\xi_0^W$

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Models of dynamic wetting

Classic hydrodynamic Model\(^1\)

\[ \theta_m = \theta^0 \]

Shikhmurzaev model\(^2\)

\[ \gamma_{LV} \]

MKT


As it seems likely that both types of dissipation occur simultaneously, combined theories have been suggested. For example in the case of a spreading drop, it has been predicted and confirmed that the wetting-line friction regime precedes the viscous regime, which becomes dominant only as the contact angle becomes small.

\[
\nu = \frac{\gamma (\cos \theta_0 - \cos \theta)}{\zeta + 6\eta \Phi[(\theta)] \ln \left(\frac{R}{a}\right)}
\]

\[
\Phi[(\theta)] = \frac{\sin^3 \theta}{2 - 3 \cos \theta + \cos^3 \theta}
\]
Petrov combined model

\[ \theta_d^3 = \arccos^3 \left[ \cos \theta_0 - \frac{2k_B T}{\lambda^2 \gamma} \ln \left( \frac{V}{2K_0 \lambda} + \sqrt{\left( \frac{V}{2K_0 \lambda} \right)^2 + 1} \right) \right] + \frac{9 \eta V}{\gamma} \ln \left( \frac{L}{L_s} \right) \]

Distribution of \(K_0\) and \(\lambda\) parameters for the OMCTS/AF1600 system
G-dyna

D. Seveno, A. Vaillant, R. Rioboo, H. Adão, J. Conti et J. De Coninck,
Molecular Dynamics
Molecular dynamics

**Advantages**
- Able to model systems at molecular level to illuminate mechanisms and yet reproduce global system behavior. Tool can therefore be to test dynamic wetting models at all scales.
- Interactions/properties can be changed independently and at will

**Disadvantages**
- Systems still small and subject to thermal fluctuations (<0.1\(\mu\)m)
- Short time scales (<1 \(\mu\)s)
- Simple, non-specific interactions (Lennard-Jones), usually truncated at short range
- Liquids tend to have low densities, surface tensions and viscosities

**Other simplifications**
- Solid surfaces are molecularly smooth and homogeneous by design - so no pinning or contact angle hysteresis
Molecular dynamics - basics

Liquid ($L$): flexible 8-atom chains (up to 421,008 atoms)  
Solid ($S$): square planar lattice with 3 atomic layers (~66,102 atoms)

Lennard-Jones intermolecular potential:

$$U_{ab} = 4\varepsilon_{ab} \left( C_{ab} \frac{\sigma_{ab}}{r_{ij}} \right)^{12} - D_{ab} \left( \frac{\sigma_{ab}}{r_{ij}} \right)^6$$

- Repulsive
- Attractive

Cutoff radius $2.5\sigma$
- $C_{SS} = C_{LL} = D_{SS} = D_{LL} = 1$
- $C_{SL} = D_{SL} = 0.2$ to $1.3$

$\varepsilon_{ab} = 4.6 \times 10^{-22}$ J, $\sigma_{ab} = 3.5\text{Å}$ for all $L-L$, $S-S$ and $L-S$ interactions

Binding potential between liquid atoms in a given molecule:

$$U_{\text{conf}}(r_{ij}) = Ar_{ij}^6 \left( A = \varepsilon_{LL} / \left( \sigma_{LL} \right)^6 \right)$$

Integrity of solid maintained with a harmonic potential:

$$U_H = B\left(r_i - r_i^0\right)^2, \quad B = 2.5\varepsilon_{SS} \left( \sigma_{SS} \right)^2$$

Lattice spacing: $2^{1/6} \sigma_{SS} = 3.93$, $n = 6.47 \times 10^{14} \text{cm}^{-2}$

Atomic mass 12 g/mol (≡ carbon) for both $L$ and $S$. $T = 33.3$ K

Time step between iterations 0.005 ps

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Molecular dynamics - example

Snapshot at 10 ns, coupling \( C_{SL} = D_{SL} = 0.6 \)
System at equilibrium
Results - density distribution of liquid at $S-L$ interface

Equilibrium data for liquid drop containing 5,000 molecules

$C_{SL} = D_{SL}$

1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2

Density (atom Å$^{-3}$)

$z$-position (Å) - solid surface at $z \sim 9\text{Å}$
Results - spreading drops

Detail at short times and low-moderate couplings

$\theta^0$ (deg)

$C_{SL} = D_{SL}$

Contact angle (deg)

Time (ns)

Snapshots at 10 ns

(5,000 molecules)
Results - spreading drops

Longer times and higher couplings

\[ C_{SL} = D_{SL} \]

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## Analysis

### For each coupling
- Measure drop radius and contact angle as a function of time.
- Calculate contact-line speed from radius data.
- Fit data with MKT.
- Calculate $\kappa_0$ and $\lambda$ from fit (or obtain $\lambda$ from simulation = 0.43 nm - see later).

### Results

<table>
<thead>
<tr>
<th>Material properties</th>
<th>$C_{SL}=D_{SL}$</th>
<th>$\theta^0$/deg</th>
<th>$\kappa^0/10^{10}$Hz</th>
<th>$\zeta_{CL}^0$/mPa s</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho_S = 364$ kg m$^{-3}$</td>
<td>0.20</td>
<td>165.9</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>$\rho_L = 341$ kg m$^{-3}$</td>
<td>0.25</td>
<td>156.7</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>$\gamma_{LV} = 2.49$ mN m$^{-1}$</td>
<td>0.30</td>
<td>147.2</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>$\eta_L = 0.248$ mPa s</td>
<td>0.35</td>
<td>141.6</td>
<td>6.550</td>
<td>0.089</td>
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<td></td>
<td>0.40</td>
<td>134.8</td>
<td>3.700</td>
<td>0.157</td>
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<td></td>
<td>0.45</td>
<td>128.7</td>
<td>2.620</td>
<td>0.222</td>
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<td></td>
<td>0.50</td>
<td>121.3</td>
<td>2.740</td>
<td>0.212</td>
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<td></td>
<td>0.55</td>
<td>114.3</td>
<td>2.300</td>
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<td></td>
<td>0.60</td>
<td>105.8</td>
<td>1.600</td>
<td>0.364</td>
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<td></td>
<td>0.65</td>
<td>99.8</td>
<td>1.250</td>
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<td>0.70</td>
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<td>0.868</td>
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<tr>
<td></td>
<td>1.10</td>
<td>0.0</td>
<td>0.528</td>
<td>1.100</td>
</tr>
</tbody>
</table>
Solid surface energy landscape

Map of the potential energy due to Lennard-Jones interactions for a single liquid atom at distance $\sigma$ from the solid surface for $C_{SL}=D_{SL}=1.0$. Adsorption sites are the potential energy wells (blue) located between the solid atom sites (red).
Solid surface energy landscape

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Probability distribution of jump distances in layer 1

Data averaged over 500 runs with 5,000 atoms from first layer of 40,000 atom drop

Couplings $C_{SL} = D_{SL} = 1.0$ (■), $0.8$ (○) and $0.6$ (▲)
Probability distribution of jump times for layer 1

Data averaged over 500 runs with 40,000 atom drop
Couplings $C_{SL} = D_{SL} = 1.0$ (A), 0.8 (B) and 0.6 (C)
Average of distribution inverted to give $\kappa_\perp$ and $\kappa_\parallel$
Comparison of measured jump frequencies $\kappa_\perp$ and $\kappa_\parallel$ with $\kappa^0$

Good agreement between $\kappa^0$ and $\kappa_\perp$ for $C_{SL} = D_{SL} > 0.4$ ($\theta^0 < 130^\circ$)

Low density effect at smaller couplings?
S-L interfacial relaxation

Start: \( C_{SL} = D_{SL} = 0.2 \)  
End: \( C_{SL} = D_{SL} = 1.1 \)

\[
\Delta \rho = \rho_{1.1} + \left( \rho_{0.2} - \rho_{1.1} \right) \exp \left( -\frac{t}{\tau_{\text{relax}}} \right)
\]

\( \tau_{\text{relax}} = 0.038 \) ns;  
\( \kappa_{\text{relax}} = \frac{1}{\tau_{\text{relax}}} \times 2.6 \times 10^{10} \text{ Hz} \);  
\( \kappa^{0}(0.5) = 2.7 \times 10^{10} \text{ Hz} \)

Max relaxation length = \( U_{\text{max}} / \tau_{\text{relax}} = 10 \text{ ms}^{-1} \times 0.038 \text{ ns} \sim 4 \text{ Å}, i.e. within TPZ! \)
Influence of solid-liquid (S-L) interactions
Molecular-kinetic theory - effect of S-L interactions on $\kappa^0$

$$\kappa^0_W = \left( \frac{k_B T}{\eta_L v_L} \right) \exp \left( -\frac{Wd_{SL}^0}{nk_B T} \right)$$

- $v_L = $ segment vol. $5.48 \times 10^{-23}$ cm$^3$
- $n = 6.47 \times 10^{14}$ cm$^{-2}$

Data from spreading drops

MKT

$Wd_{SL}^0 = \gamma_{LV} (1 + \cos \theta^0)$ (mJm$^{-2}$)
Molecular-kinetic theory - effect of S-L interactions on $\zeta_{CL}^0$

$$\zeta_{CL}^0 = \frac{\eta_L v_L}{\lambda^3} \exp \left( \frac{W a_{SL}^0}{n k_B T} \right)$$

Data from spreading drops

$\ln \left( \frac{\zeta_{CL}^0}{\text{Pas}} \right)$

Data from simulation

Eq (2.10)

$v_L = \text{segment vol.}$

$5.48 \times 10^{-23} \text{ cm}^3$

$n = 6.47 \times 10^{14} \text{ cm}^{-2}$

$W a_{SL}^0 = \gamma_{LV} (1 + \cos \theta^0)$ (mJm$^{-2}$)
Influence of $S-L$ interactions: Experimental results\textsuperscript{5}

Logarithm of contact-line friction coefficient normalised for the liquid viscosity versus work of adhesion for various liquids wetting Nylon-6 filament.

The straight line is the best fit to the MKT:

\[
\frac{\xi_{CL}^0}{\eta_L} = \frac{v_L}{\lambda^3} \exp \left( \frac{Wa_{SL}^0}{nk_B T} \right)
\]

\textsuperscript{5} Vega, et al., \textit{Langmuir} 23 (2007), 10628

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Influence of S-L interactions: Experimental results\textsuperscript{6}

Logarithm of contact-line friction coefficient normalised for the liquid viscosity versus work of adhesion for water wetting
(a) OTHS on titania and
(b) Long-chain thiols on gold.

The straight lines are the best fits to the MKT:

\[
\frac{\zeta_{CL}}{\eta_L} = \frac{\nu_L}{\lambda^3} \exp \left( \frac{W a_{SL}^0}{n k_B T} \right)
\]

\textsuperscript{6} Ray, Sedev, Priest & Ralston, \textit{Langmuir} 24 (2008) 13007
Effect of equilibrium contact angle on maximum velocity of wetting $U_{\text{max}}$

\[ U = U_{\text{max}} \cos \phi \]  
Saw-tooth wetting line forms when $U > U_{\text{max}}$.

Air entrained from trailing vertices

MKT predicts competing effects:

\[ U_{\text{max}} = \frac{2k_B T \lambda}{\eta_L v_L} \exp \left[ \frac{-W_{\text{SL}}^0}{nk_B T} \right] \sinh \left[ \frac{\gamma_L v_L}{2nk_B T} \cos \theta^0 + 1 \right] \]

Smaller contact angle increases friction
Smaller contact angle increases driving force

Curve calculated for water assuming $\lambda = 0.36$ nm

Air-entrainment speed for water on PET tape

7 Blake & Ruschak, Nature 282 (1979), 489
Effect of substrate wettability on maximum coating speed envelope

Substrates: PET coated with gelatin containing various surfactants (non-ionics, anionics, alkyl and aryl hydrocarbon, and fluorocarbon).

Contact angles: calculated from the surface free energy components of the substrates as determined by method of Owens and Wendt.

Coating speeds: determined by curtain coating 15% aqueous gelatin solution: flow rates 3.0-3.5 cm²s⁻¹, curtain height 3 cm, viscosity ~70 mPas.

Effect of coupling on dynamic contact angle

Curves calculated with fitted values of $\kappa^0$ and $\lambda = 0.43$ nm
Effect of equilibrium contact angle on maximum velocity of wetting $U_{\text{max}}$

$U_{\text{max}} / \text{ms}^{-1}$

Results from MD simulations

MKT prediction

Equilibrium contact angle (deg)
Other evidences
Other experimental evidences

Saiz+Tomsia, Nature Materials, 2004
Dynamic contact angle as a function of capillary number for a silicone-air interface: open circles, 47V5000 oil-air interface in a precision bore tube; full circles, 47V5000 oil-air interface in a standard capillary tube; open triangles, Hoffman’s data; full lines, Cox’s theory with $\varepsilon=10^{-7}$ (1), $10^{-6}$ (2), $10^{-5}$ (3) and $10^{-4}$ (4). From Fermigier et al., 1991

Small angle theory valids up to $\theta = 100^\circ$ and $\text{Ca} = \eta U / \gamma = 10^{-1}$

Fermigier et al., 1991
To simulate a solid moving at constant speed, iterative shifts are applied to the reference f.c.c. lattice configuration at each time step with appropriate periodic boundary conditions.

The analysis of the contact angle data reveals apparently two regimes in perfect agreement with Brochard-de Gennes observations:

- the hydrodynamic regime which describe well the data at low speed and
- the molecular-kinetic regime which works well here since the associated steady contact angles $\theta_e$ are rather large.
Coating of a moving fiber
Conclusions

• Large-scale MD provides a useful approach to modelling the impact of S-L interactions on wetting and spreading of liquids on solids.

• MK parameters obtained by fitting data ($\kappa^0$ and $\lambda$) agree with those obtained directly from the atomistic dynamics of the simulations, thus validating the MKT at some fundamental level.

• S-L interactions effect density near the wall (layering). First layer dynamics dominate dynamic wetting behaviour.

• Wetting dynamics reflect the retarding influence of the energy landscape of the solid surface. Jump distance $\lambda$ is determined largely by the spacing of the energy wells and independent of their depth. However, the jump frequency $\kappa^0$ is controlled by the depth of the wells.

• MD and Experimental results show that the MKT not only models dynamic wetting in these simple systems, but successfully accounts for at least the qualitative effect of S-L interactions.

• The practical implication is that surfaces can be engineered not only for their static wettability and adhesion, but for their wetting dynamics.

• For any process there is likely to be an optimum static angle that maximizes the speed of wetting/dewetting and the rearrangement of liquids on surfaces.
Questions?