Relaxation of Surface Tension in the Liquid–Solid Interfaces of Lennard-Jones Liquids

Alex V. Lukyanov* and Alexei E. Likhtman

School of Mathematical and Physical Sciences, University of Reading, Reading RG6 6AX, U.K.

ABSTRACT: We have established the surface tension relaxation time in the liquid–solid interfaces of Lennard-Jones (LJ) liquids by means of direct measurements in molecular dynamics (MD) simulations. The main result is that the relaxation time is found to be almost independent of the molecular structures and viscosity of the liquids (at 70-fold change) used in our study and lies in such a range that in slow hydrodynamic motion the interfaces are expected to be at equilibrium. The implications of our results for the modeling of dynamic wetting processes and interpretation of dynamic contact angle data are discussed.

I. INTRODUCTION

The wetting of solid materials by a liquid is at the heart of many industrial processes and natural phenomena. The main difficulty in the theoretical description and modeling of wetting processes is the formulation of boundary conditions at the moving contact line.1–3 For example, the standard no-slip boundary condition of classical hydrodynamics had to be relaxed to eliminate the well-known nonintegrable stress singularity at the contact line.4–5

The principal parameter of the theoretical description is the dynamic contact angle, which is one of the boundary conditions used to determine the shape of the free surface.1–5 The notion of the contact angle has two meanings in macroscopic modeling. One is the apparent contact angle \( \theta_a \), which is observed experimentally at some distance from the contact line defined by the resolution of experimental techniques (usually a few micrometers), and another one is the true contact angle \( \theta \) right at the contact line. When the contact line is moving, the apparent contact angle deviates from its static values and becomes a function of velocity. For example, quite often the contact-angle-velocity dependence \( \theta_a(U) \) observed in experiments can be accurately described by

\[
\cos \theta_a = \cos \theta_0 - a_1 \sinh^{-1}(a_2 U)
\]

(1)

where \( a_1 \) and \( a_2 \) are material parameters depending on the temperature and properties of the liquid–solid combination, \( U \) is the contact-line velocity, and \( \theta_0 \) is the static contact angle.3 However useful eq 1 may be, it is neither general, due to the well-known effects of nonlocality,3,6,7 nor can be directly used in macroscopic modeling because it is the true contact angle that enters the boundary conditions used in macroscopic analysis. Although the apparent contact angle can be experimentally observed, the true contact angle can be inferred only from theoretical considerations or from microscopic modeling such as MD simulations. This is one of the main problems in wetting hydrodynamics, and that problem, despite decades of research, is still far from being completely understood. The main question remains open, and debate continues: how (and why) does the true dynamic contact angle change with the contact-line velocity?

The simple hypothesis of \( \theta = \theta_0 \) has been used in the so-called hydrodynamic theories, for example in ref 8, where the experimentally observed changes in the apparent contact angle were attributed to viscous bending of the free surface in a mesoscopic region near the contact line. Some early observations of the meniscus shapes at the contact line have indicated that indeed the meniscus curvature may strongly increase at the contact line.9 The subsequent analysis has shown that, whereas the dynamic contact angle effect may be purely apparent in some cases, it was difficult to rule out variations in the true contact angle. Later on, a numerical study of slip models showed that, whereas viscous bending can contribute to the observed changes in the apparent contact angle, this effect alone is insufficient to explain the observations.10 Moreover, recent MD simulations of the spreading of LJ liquid drops have shown that the true contact angle does change with the velocity and produces a contact-line-velocity dependence similar to that in eq 1.11–13

The results of MD simulations have been successfully compared against the molecular-kinetic theory (MKT).11,12 In the MKT, which is also in good agreement with experiments,3 the true contact angle is a function of velocity. This velocity dependence comes from the difference in the probability (asymmetry) of molecular displacements parallel to the solid substrate at the moving contact line, according to the phenomenological assumptions made in the model. The asymmetry is propor-
tional to the contact-line velocity and to the work done by a macroscopic out-of-balance surface tension force \( f_s = \gamma_{SV} (\cos \theta_s - \cos \theta) \) acting on the contact line. The net result is (1) \( \alpha_i = 2k_B T / \gamma_{SV} \lambda_i^2 \), \( \lambda_i = (2 \kappa^2 \lambda_i^2)^{-1} \), where \( \gamma_{SV} \) is the surface tension at the liquid–gas interface, \( k_B \) is the Boltzmann constant, \( T \) is the temperature, and \( \kappa \) is the frequency of displacements over the distance \( \lambda \), which is regarded as the inverse relaxation time of the surface phase \( (k^0)^{-1} = \tau_{LS} \), which is supposed to be proportional to the viscosity \( \tau_{LS} \propto \mu \). The key feature of the model is the concentrated force \( f_s \) acting on the contact line, similar to the resistive force introduced in ref 14, so that the MKT is local.

Because the MKT is local, it would be difficult to explain effects of nonlocality solely within the model. A more general and potentially universal approach to modeling the dynamic wetting, the interface formation theory, has been proposed by Shikhmurzaev.1,2 The self-consistent macroscopic approach naturally introduces the dynamic contact angle through dynamic values of surface tension on forming liquid–solid interfaces. The approach is very appealing and has shown excellent agreement with experimental observations15 but requires a knowledge of the macroscopic surface tension relaxation time \( \tau_{LS} \) of the liquid–solid interface, which is also supposed to be proportional to the viscosity \( \tau_{LS} \propto \mu \). As consequence, the theory is truly nonlocal, that is, able to explain the effects of nonlocality2,7,16,17 with the key characteristic feature, the relaxation time of the dynamic surface tension on the length scale \( \sim U_{LS}(CaSc)^{-1} \), \( Ca = \mu U_{LS}/Sc \approx S/(\tau_{LS}/6 \times 10^{-9}) \sim 1.5 \times 10^{-3} \) Pa s/\( \mu \)^{1/2}, a nondimensional material parameter defining the strength of the interface formation effect \( \cos \theta_s - \cos \theta \propto CaSc \).15

In summary, we have at least two principally different models of dynamic wetting, and both of them seem to be in very good agreement with experimental data.3,15 However, which mechanism actually determines the dynamic contact angle? To what extent can the dynamic interfaces be in non-equilibrium conditions and contribute into the dynamic contact angle effect?

The key to answering these questions appears to be the surface tension relaxation time \( \tau_{LS} \) of the liquid–solid interface, and in this Letter, we directly establish this fundamental parameter by MD simulations. The simulations have been conducted in a model system consisting of LJ particles and/or chain molecules. We investigate the \( \tau_{LS} \) dependence on liquid viscosity and temperature and conduct direct MD experiments with the dynamic contact angle to gain insight into the mechanism of dynamic wetting.

II. MODEL

The MD model we use is similar to that in ref 18 but with LJ potentials \( \Phi_{ij}(r) = 4\epsilon_{ij}(\sigma_{ij}/r)^12 - (\sigma_{ij}/r)^6 \) and the cutoff distance 2.5\( \sigma_{ij} \). Here, \( i \) and \( j \) are either 1 or 2 to distinguish between liquid and solid wall particles with masses \( m \). Note that hereafter all units are nondimensional, the length is measured in \( \sigma_{ij} \), the energy and temperature are measured in \( \epsilon_{ij} \), the mass is measured in \( m_{ij} \) and the time is measured in \( \sigma_{ij}^2/(m_{ij}\epsilon_{ij})^{1/2} \). The beads interacting via LJ potentials are connected into linear chains of \( N_b \) beads by the finitely extensible nonlinear elastic (FENE) springs, and the strength of the springs is adjusted so that the chains cannot cross each other, \( \Phi_{FENE}(x) = k/2R_0^2 \ln(1-(x/R_0)^2) \). Here, \( R_0 = 1.5 \) is the spring maximum extension, and \( k = 30 \) is the spring constant.

The idea of our MD experiment is simple and is similar to experimentally designed reversibly switching surfaces.9 First, we equilibrate a square \( (L_x = 30 \times L_z = 20) \) of a liquid film of thickness \( L_y \approx 20 \) (the \( y \) axis is perpendicular to the film surface and periodic boundary conditions are applied in the \( x, z \) directions) consisting of 12 000 particles during \( \Delta t_{eq} = 5000 \) with the time integration step \( \Delta t_{MD} = 0.01 \), which is used in the study. The temperature 0.8 \( \leq T \leq 1.2 \) is controlled by means of a DPD thermostat with friction \( \zeta_{bd} = 0.5 \). The film was positioned between two solid substrates consisting of three \( [0, 0, 1] \) fcc lattice layers of LJ atoms with the shortest distance between the beads \( \sigma_{22} \), where \( \sigma_{22} = 0.7, m_{12} = 10 \), and \( \epsilon_{22} = 0 \). The pressure in the system was kept close to the vapor pressure at a given temperature \( T \) by adjusting \( L_y \) accordingly and making the second wall potential at \( y = L_y \) purely repulsive. This has allowed for a small gap between the wall and the liquid phase to establish the gas phase. The solid wall particles were attached to anchor points via harmonic potential \( \Phi_s = \xi^2 \), with the strength \( \xi = 800 \) chosen such that the root-mean-square displacement of the wall atoms was small enough to satisfy the Lindemann criterion for melting \( \langle \delta r^2 \rangle^{1/2} < \epsilon \) (0.2).10 The anchor points in the layer of the solid wall facing the liquid molecules have been randomized in the vertical \( y \) direction to increase/vary the surface roughness. The amplitude \( \langle \delta y^2 \rangle^{1/2} = 0.1\sigma_{22} \) was shown to be sufficient to prevent the substrate from having a large, shear-rate divergent/independent actual slip length.21 The slip length measured in our experiments, as in ref 21, was \( l_{slip} \approx 2 - 4\epsilon_{11} \). After equilibration, parameter \( \epsilon_{12} \) of the wall at \( y = 0 \) is changed from one value to another, and we observe the relaxation of interfacial parameters, including the surface tension.

The surface tension of a plane liquid–solid interface is calculated according to ref 22 on the assumption of the rigid solid substrate:

\[
\gamma_{LS} = \lim_{\gamma_{SV} \to \infty} \int_0^{\gamma_{SV}} \left\{ T_i - T_n - \gamma \rho(y) \frac{dy}{dy} \right\} dy
\] (2)

Here, \( \rho(y) \) is the distribution of density, \( \gamma \rho(y) \) is the substrate potential generated by the solid wall particles, \( T_i(y) \) are the tangential and normal components of the microscopic stress tensor evaluated according to ref 23 in which all quantities are averaged in the \( (x, z) \) plane. We note here that eq 2 is an approximation in our case of the weakly rough wall consisting of moving particles,12,24,25 Therefore, the numerical procedure has been verified using the Young–Dupré equation by placing a substantially large cylindrical liquid drop (about 30 000 particles) on the solid substrate and measuring the static contact angle \( \theta_b \) by applying a three-parameter circular fit \( (y-y_0)^2 + (z-z_0)^2 = R^2 \) to the free surface profile. The free-surface profile was defined in the study as the locus of equilibrium points. The obtained values of \( \theta_b \) were found to be within \( 3^\circ \) of the contact angles calculated directly from the Young–Dupré equation using independently evaluated values of the surface tension. The liquid–gas \( \gamma_{SV} \) surface tension has been calculated using large liquid drops \( (radius \sim 30) \), similar to those in ref 26. Typical dependencies of the integral in eq 2, \( \gamma_{LS}(\theta_b) \), under static conditions are shown in Figure 1 at different values of \( \epsilon_{12} \).

III. RESULTS AND DISCUSSION

In the dynamic experiments, parameter \( \epsilon_{12} \) was switched from 0.2 to 0.65 (equivalently \( \theta_b = 165 \) to \( 90^\circ \) at \( T = 0.8 \), \( N_b = 5 \)) during \( \Delta t_i = 1 \) with fixed \( \sigma_{12} = 0.7 \). The evolution of the surface
data reveals applied to an average of normalized surface tension evolution relaxation is very quick and almost independent of the liquid plain geometry) and dynamic (slug geometry, Figure 4, averaged over $\Delta z = 10$ at the contact line, $U = 0.1$, and $\gamma_{12} = 0.9$) conditions for a liquid with $N_B = 5$ at $T = 0.8$. The dashed line shows the surface tension level at $\theta_0 = 138^\circ$.

Figure 1. Profiles of the integral in eq 2 under static (at $\gamma_{12} = 0.9$, $\tau_{LS}(S) = -0.89$, $\theta_0 = 15^\circ$, and $\gamma_{12} = 0.37$, $\tau_{LS}(S) = 0.68$, $\theta_0 = 138^\circ$, in plain geometry) and dynamic (slug geometry, Figure 4, averaged over $\Delta z = 10$ at the contact line, $U = 0.1$, and $\gamma_{12} = 0.9$) conditions for a liquid with $N_B = 5$ at $T = 0.8$. The dashed line shows the surface tension level at $\theta_0 = 138^\circ$.

Figure 2. Relaxation of liquid—solid surface tension (integrated to $y_s = 5$) at different temperatures $T$ and molecular compositions $N_B$ after switching the interaction parameter $\gamma_{12}$ from 0.2 to 0.65 at $t_0 = 100$ during $\Delta t_1 = 1$. The data are averaged over $\Delta t_1 = 1$ and 200 independent experiments. The dashed line is fit $f_{1,0} = 7.8$, applied to an average of all four profiles. The inset shows the individual dependence at $T = 0.8$ and $N_B = 5$. The solid (red) line in the inset is fit $f_{1,0}$.

Figure 3. Evolution of the density distributions $\rho(y, t)$ (main plot) and surface density $\rho^s(t) - \rho(0))/\rho(0)$ (inset) at $T = 0.8, N_B = 5$ after switching interaction parameter $\gamma_{12}$ from 0.2 to 0.65 at $t_0 = 100$ during $\Delta t_1 = 1, \Delta t = t - t_0$. The solid (red) line in the inset is fit $f_{1,0}$.

tension, density distribution, and surface density $\rho' = (\rho(1 + f_{1,0}))^{-1}$

$\int_0^{\infty} \rho(y) dy$ is shown in Figures 2 and 3 for different liquid compositions and temperatures. One can see that in general the relaxation is very quick and almost independent of the liquid viscosity at first glance (the results are insensitive to lowering $\varepsilon_{bpd}$ to 0.3). A simple fit $f_{1,0} = C_1 + C_2 \exp(-t - t_0)/\tau_{1,0}$, applied to an average of normalized surface tension evolution data reveals $\tau_{1,0} = 7.8$ (Figure 2). The individual dependencies (inset of Figure 2) reveal more complex behavior, which can be approximated by $f_1 = C_1 + C_2 \exp(-(t - t_0)/\tau_1) + C_3 \exp(-(t - t_0)/\tau_2) \sin(\omega(t - t_0) + \phi_0)$ (Table 1). One can see that both $\tau_1$ and $\tau_2$ are almost independent of the molecular structure/viscosity despite the 70-fold variation in $\mu$. The observed values of $\tau_1$ (the major relaxation) are close to the relaxation times found in the free surfaces of LJ liquids, and thus correspond to the local relaxation on the length scale of the individual density peaks (Figure 3), that is, on the bead level rather than on the level of whole molecules. This is similar to the multiscale relaxation commonly observed in polymer dynamics. In our case, initial, early-time relaxation is defined by the mean square displacement of individual monomers over a relatively short distance on the order of half the distance between the density peaks ($\Delta y = 0.5$) (Table 1) whereas the liquid viscosity is defined by the much slower molecular relaxation. This is also consistent with the weak dependence on the destination value $\gamma_{12}(t > t_0)$ (Table 1, last row).

The second, oscillatory relaxation, $\tau_2$ at frequency $\omega$, is likely to be due to the collective excitation of the particle motion triggered by the sharp change in the solid wall potential because the amplitude of oscillations decreases with increases in the switching time interval $\Delta t_1$. In this case, $\tau_2$ is simply the time during which the excited wave of frequency $\omega$ travels some distance $l_\omega$ comparable to the interfacial layer width. Indeed, the product $t_0\omega = 2\pi l_\omega/\lambda_\omega$, where $\lambda_\omega$ is the wavelength, varies within $3.1 \leq t_0\omega \leq 5.8$, where $t_0\omega = 4.4$ (Table 1). Then on average $\langle l_\omega/\lambda_\omega \rangle \simeq 0.7$, which means that the wavelength of the excitations is roughly the width of the interfacial layer.

We note that the observed weak dependence $\tau_{2,0}(\mu)$ is in contrast to the relaxation time scaling $\tau_{LS} \propto \mu$ found in the MKT and in the interface formation theory. Although the first peak density characteristic time scale found in the MD simulations $t_{dp} \approx 16.5$ is roughly comparable to our results (Table 1), the observed weak dependence $\tau_{2,0}(\mu)$ rules out possible connections between $\tau_{LS}$ and MKT parameter $(k')^{-1}$.

The relaxation times revealed by the dynamic experiments directly imply that in the liquid compositions used in our study, for the slow hydrodynamic motion, parameter $U t_{LS}/L \ll 1$ ($L \gg 1$ is any macroscopic length scale and $U \ll 1$ is hydrodynamic velocity or the substrate velocity) and the surface tension is expected to be at equilibrium. This in turn implies that the dynamic surface tension is unlikely to be the cause of the dynamic contact angle in our case, interface formation parameter $Sc \ll 1$. To verify this conclusion, we have performed a series of MD experiments with a large cylindrical liquid slug (60 000 particles) forced between two identical rough solid plates (Figure 4). The geometry is periodic in the $x$ direction with reflective boundary conditions at the simulation box ends in the $z$ direction. The solid wall particles are moving
Table 1. Parameters of the Liquids\(^a\) and Characteristic Times of Liquid–Solid Interface Formation\(^b\) at Different Molecular Compositions\(^c\) and Temperatures \(T\)

<table>
<thead>
<tr>
<th>(T)</th>
<th>(N_b)</th>
<th>(\gamma_{LV})</th>
<th>(\rho_b)</th>
<th>(\mu^\alpha)</th>
<th>(\tau_1)</th>
<th>(\tau_2)</th>
<th>(\omega)</th>
<th>(\tau_f)</th>
<th>(\omega^*)</th>
<th>((\langle\tau_M^2\rangle)^{1/2})</th>
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<tr>
<td>0.8</td>
<td>1(^d)</td>
<td>0.36 ± 0.02</td>
<td>0.73</td>
<td>1.2</td>
<td>2.4 ± 0.6</td>
<td>15.3 ± 2.2</td>
<td>0.20</td>
<td>5.5 ± 0.5</td>
<td>16.1 ± 0.4</td>
<td>0.20</td>
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<tr>
<td>0.8</td>
<td>5</td>
<td>0.92 ± 0.04</td>
<td>0.91</td>
<td>10.5</td>
<td>3.9 ± 0.3</td>
<td>10.7 ± 0.8</td>
<td>0.43</td>
<td>3.8 ± 0.1</td>
<td>9.3 ± 0.2</td>
<td>0.39</td>
</tr>
<tr>
<td>0.8</td>
<td>10</td>
<td>1.01 ± 0.05</td>
<td>0.93</td>
<td>20.2</td>
<td>4.3 ± 0.3</td>
<td>9.2 ± 0.7</td>
<td>0.48</td>
<td>3.6 ± 0.1</td>
<td>8.7 ± 0.2</td>
<td>0.44</td>
</tr>
<tr>
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<td>0.93</td>
<td>30.1</td>
<td>5.6 ± 1.2</td>
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<td>12.1 ± 0.5</td>
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</tr>
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<td>3.7 ± 0.1</td>
<td>8.3 ± 0.2</td>
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\(^{a}\)Equilibrium surface tension \(\gamma_{LV}\), bulk density \(\rho_b\), and dynamic viscosity \(\mu\). The viscosity was obtained as in ref 27 under bulk conditions. The last column is the end-monomer mean-square displacement during \(\Delta t = \tau_1\) across the interface under the bulk conditions. \(^{b}\)\(\tau_{1,2,\omega}\) for the surface tension and \(\tau_{f,\tau}^o\) for the surface density \(\rho^o\) applying fit \(f_1\). \(^{c}\)Number of beads \(N_b\). \(^{d}\)Four hundred independent experiments. \(^{e}\)\(\epsilon_{12}(t > t_0) = 0.9\).

Figure 4. Snapshots and free surface profiles (circular fits) in static and dynamic (\(U = 0.1\)) situations at \(T = 0.8, N_b = 5, \text{and} \epsilon_{12} = 0.9 (\theta_0 = 15^\circ)\). The observed static and dynamic contact angles are \(\theta_0 = 12 \pm 3^\circ\) and \(\theta_0 = 138 \pm 4^\circ\), respectively. The direction of the moving solid wall particles is indicated by the arrow.

Figure 5. Density distribution at different distances from the contact line \(\Delta z\) averaged over \(\Delta z = 1.25\) in the dynamic case shown in Figure 4 at \(U = 0.1, \epsilon_{12} = 0.9\) (slug geometry), and under static conditions (plain geometry) at \(T = 0.8, N_b = 5, \epsilon_{12} = 0.9 (\theta_0 = 15^\circ)\), and \(\epsilon_{12} = 0.37 (\theta_0 = 138^\circ)\).

with velocity \(U\) in the \(z\) direction to mimic the forced wetting regime. After initial equilibration during \(\Delta t_{eq} = 5000\), we measure the dynamic contact angle and interface parameters under steady conditions. The dynamic contact angle can be clearly seen in the snapshot and in the developed free surface profile (Figure 4). This is an extreme case (\(Ca = 1.1\)) of typical profiles observed in the case of long-chain molecules when the dynamic contact angle \(\theta\) is changing monotonically with the substrate velocity \(U\) from its equilibrium value. We have checked that the system size has no dramatic effect on the observed contact angle. For example, in a similar case \(\epsilon_{12} = 0.65, \theta_0 = 90^\circ, U = 0.1\); at 60 000 particles, \(\theta = 143.7 \pm 3^\circ\); at 40 000 particles, \(\theta = 142.4 \pm 3^\circ\); and at 10 000 particles, \(\theta = 129 \pm 3^\circ\).

The direct measurements of surface tension and the distribution of density, in the case shown in Figure 4, right after the contact line, are shown in Figures 1 and 5. The contact line width is taken at \(\Delta z = 6\) counting from the intersection of the free surface and the substrate at \(z_{c1} = 0, \) Figure 4, just to cover the interfacial zones of both interfaces fully. One can see that indeed whereas the liquid motion has some effect on the first layer of particles, the overall effect is not large and both the surface tension and the density are close to equilibrium and far away from the values in the case of \(\epsilon_{12} = 0.37 (\theta_0 = 138^\circ)\) similar to the observed dynamic angle). How had that dynamic angle (different from \(\theta_0 = 15^\circ\)) been generated? We analyzed the tangential force acting on the interface molecules in the region \(0 \leq y \leq y_m = 2, z_{c1} \leq z \leq z_{c1} + \Delta z_1\) at the contact line. We found that the tangential force \(f_{12}^T\) acting on the liquid from the solid substrate is concentrated within \(\Delta z_1\) and then decreases significantly. This is not a coincidence, of course, because \(\Delta z_1 \approx l_{dyne}\). The value of the force per unit length of the contact line is found to be sufficient to generate the observed contact angle according to the balance of all forces acting on the contact line, the modified Young–Dupré equation, that is, \(f_{12}^T = 1.52 \pm 0.13\) and from \(\gamma_{LV} \cos(\theta) = -f_{12}^T - f_{12}^z, \theta = 133 \pm 10^\circ\). This effect requires further study.

IV. CONCLUSIONS

We have directly established the relaxation time of the liquid–solid interfaces in a model system consisting of LJ molecules. The relaxation time, importantly, appears to depend very weakly on the molecular structure and viscosity (at 70-fold change) and is found to be in such a range that interfacial tension \(\gamma_{LS}\) should be in equilibrium in slow hydrodynamic motion. This has been also verified in the MD experiments on dynamic wetting, where the dynamic contact angle was
observed. Our results have direct repercussions on the theoretical interpretation and modeling of the dynamic contact angle. Although a question remains open: to what degree will our results be applicable to the liquids consisting of real molecules and when would we observe the dynamic tension associated with the effects of nonlocality?

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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