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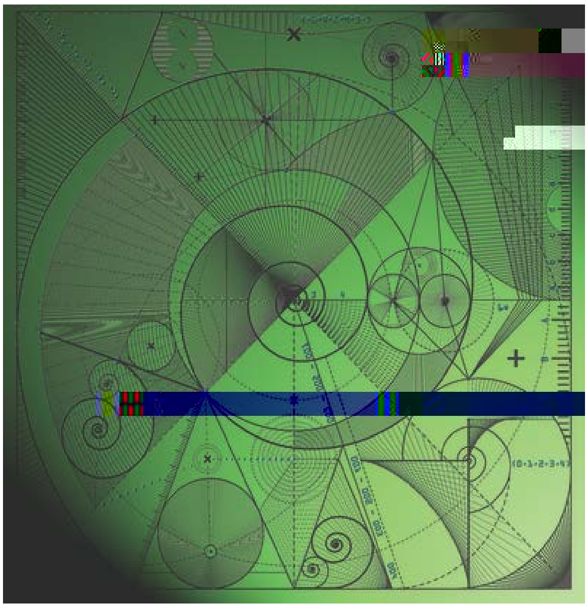

Relaxation of surface tension in the liquid-solid interfaces of Lennard-Jones liquids: Dynamic surface tension - myth or reality?

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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 weakly dependent on the molecular structures 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 modelling of dynamic wetting processes and interpretation of dynamic contact angle data are discussed.

The wetting of solid materials by a liquid is at the heart of many industrial processes and natural phenomena. The main difficulty in theoretical description and modelling 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 non-integrable stress singularity at the contact line [1{5].

The principal parameter of the theoretical description is the dynamic contact angle, which is one of the boundary conditions to determine the shape of the free surface [1{3]. The notion of the contact angle has two meanings in macroscopic modelling. One is apparent contact angle $_a$, which is observed experimentally at some distance from the contact line defined by the resolution of

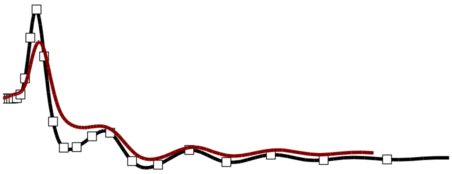

FIG. 1: Profiles of the integrand of (2) in static (at $_{12}$ = 0:9, $_{LS}$(5) = 0:89, $_{0}$ = 15 , and $_{12}$ = 0:37, $_{LS}$(5) = 0:68, $_{0}$ = 138 , in the plain geometry) and dynamic (slug geometry, Fig. 4, averaged over z

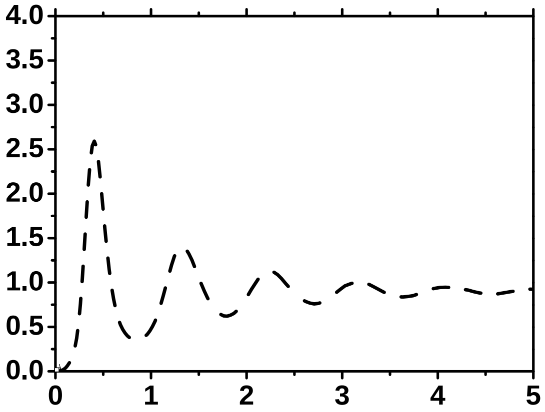

FIG. 3: Evolution of the density distributions (y; t), the main plot, and surface density ($^s(t)$ $^s(0)) = {}^s(0)$, the inset, at T = 0:8, N_B = 5 after switching the interaction parameter $_{12}$ from 0:2 to 0:65 at t_0 = 100 during t_s, t = t t_0. The solid (red) line in the inset is t f_1.

tached to anchor points via harmonic potential $_a = \ x^2$, with the strength = 800 chosen such that the root-mean-square displacement of the wall atoms was small enough to satisfy the Lindemann criterion for melting $\sqrt{< r^2 >} < 0{:}15\ _{22}$ [20]. The anchor points in the layer of the solid wall facing the liquid molecules have been randomised in the vertical y direction to increase/vary the surface roughness. The amplitude $\sqrt{< y^2 >} = 0{:}1\ _{22}$ was shown to be sufficient to prevent the substrate from having large and shear-rate divergent/dependent actual slip length [21]. The slip length measured in our experiments, as in [21], was' 2 4 $_{11}$. After equilibration, parameter $_{12}$ of the wall at y = 0 is changed from one value to another and we observe relaxation of interfacial parameters, including the surface tension.

The surface tension of a plane liquid-solid interface is calculated according to [22], in the assumption of the rigid solid substrate

$$_{LS} = \lim_{y_m\, !1} \ Z_0^{y_m} \quad T_t \quad T_n \quad y\ (y) \frac{d}{dy}\ dy: \qquad (2)$$

Here (y) is distribution of density, (y) is the substrate potential generated by the solid wall particles, $T_{t;n}$ (y) are the tangential and normal components of the microscopic stress tensor evaluated according to [23], all quantities are averaged in the (

FIG. 4: Snapshots and free surface profiles (the circular fits) in static and dynamic ($U = 0:1$) situations at $T = 0:8$, $N_B = 5$ and $_{12} = 0:9$ ($_0 = 15$). The observed static and dynamic contact angles are $_0 = 12$ 3 and = 138 4 . The direction

FIG. 5: Density distribution at different distances from the contact line z averaged over $z_a = 1:25$ in the dynamic case shown in Fig. 4 at $U = 0:1$, $_{12} = 0:9$ (slug geometry) and in static conditions (plain geometry) at $T = 0:8$, $N_B = 5$, and $_{12} = 0:9$ ($_0 = 15$) and $_{12} = 0:37$ ($_0 = 138$).

time scale found in the MD simulations [12] $_{dp}$ ' 16:5 is roughly comparable to our results, Table I, the observed weak dependence $_{1;2}$( ) rules out possible connections between $_{LS}$ and the MKT parameter (k^0) ^{1}.

The relaxation times revealed by the dynamic experiments directly imply that in the liquid compositions used in our study, in the slow hydrodynamic motion, parameter U $_{LS}$ $=L$ << 1 (L >> 1 is any macroscopic length scale) and surface tension is expected to be at equilibrium. This in turn implies that the dynamic surface tension is unlikely to be the cause of dynamic angle in our case, Sc << 1. To verify this conclusion, we have performed a series of MD experiments with a large cylindrical liquid slug (60000 particles) forced between two identical rough solid plates, Fig. 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 with velocity U in the z-direction to mimic forced wetting regime. After initial equilibration during $t_{eq} = 5000$, we measure the dynamic contact angle and interface parameters in steady conditions. The dynamic contact angle can be clearly seen in the snapshot and in the developed free surface profile, Fig. 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 is changing monotonically with the substrate velocity U from its equilibrium value. We have checked that the system size has already no dramatic effect on the observed contact angle. For example, in a similar case $_{12} = 0:65$; $_0 = 90$; $U = 0:1$, at 60000 particles = 143:7 3 , at 40000 particles, 12 smaller in the $y; z$-directions, = 141 3 , while at 10000 particles = 129 3 .

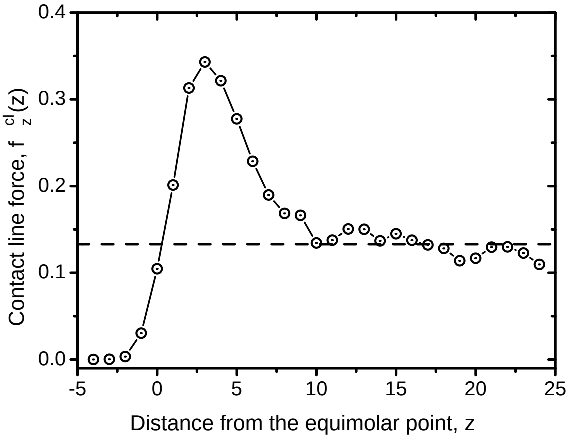

FIG. 6: Distribution of the force from the solid substrate acting on the liquid molecules in 0 y $y_m = 2$, z_{cl} z z_{cl} + $_{cl}$ in the case shown in Fig. 4 at $U = 0:1$, $_{12} = 0:9$. The dashed line indicates the mean background value.

The direct measurements of surface tension and distribution of density, in the case shown in Fig. 4, right after the contact line (the contact line width is taken at $_{cl} = 6$ counting from the intersection of the free surface and the substrate at $z_{cl} = 0$, Fig. 4, just to fully cover the interfacial zones of both interfaces) are shown in Figs. 1, 5. One can see that indeed while 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 $_{12} = 0:37$ ($_0 = 138$ similar to the observed dynamic angle). How had then that dynamic angle (different from $_0 = 15$) been generated? We analysed the tangential force acting on the interface molecules in the region (0 y $y_m = 2$, z_{cl} z z_{cl} + $_{cl}$) at the contact line. We found that the tangential force f_z^{cl} acting on the liquid from the solid substrate is concen-

T	N_B	LV	B	y	1	2	!	1	2	!	p <

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