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1 Microscopic liquid-gas interface effect on liquid wetting

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20

21 **Abstract:**

22 **Hypothesis:** Young contact angle is widely applied to evaluate liquid wetting phenomena on solid
23 surfaces. For example, it gives a truncated-spherical shape prediction of a droplet profile through
24 the Young-Laplace equation. However, recent measurements have shown deviations between
25 microscopic droplet profiles and the spherical shape, indicating that the conventional Young
26 contact angle is insufficient to describe microscopic wetting phenomena. In this work, we
27 hypothesize that a liquid-gas interface nano-bending, which is caused by the nonlinear coupling
28 between the effects of the microscopic interface geometry and solid-liquid interactions, is
29 responsible for this deviation.

30 **Simulation and theory:** Using molecular dynamics simulations and mathematical modeling, we
31 reveal the structure of the nano-bending and the mechanism of the nonlinear-coupled effect. We
32 further apply our findings to illustrate a liquid microlayer with the saddle-shaped profile in
33 nucleate boiling.

34 **Findings:** The nonlinear-coupled effect is responsible for the deviation of a nano-droplet profile
35 and also the very thin microlayer captured by different experiments. The saddle-shaped interface
36 significantly highlights the nonlinear-coupled effect. The interface nano-bending, rather than the
37 Young contact angle, acts as the boundary condition and dictates the liquid wetting system,
38 especially for the case with high interface curvature. These findings provide insight into recent
39 nano-scale droplet- and bubble-related wetting phenomena.

40 **KEYWORDS:** liquid wetting, nano-bending, nonlinear-coupled effect, interface curvature,
41 Young contact angle, nano-droplet, nano-bubble, microlayer, nucleate boiling

42 **1. Introduction**

43 Liquid wetting on surfaces is ubiquitous in nature and is of great scientific and technological
44 interest [1–4]. Recent examples such as liquid directional steering [5], surface curvature-driven
45 droplet motion [6], ultra-thin water film evaporation [7,8], and triboelectric nanogenerators [9,10]
46 have illustrated the beauty of the wetting phenomena by tailoring the solid surface properties,

47 including curvature, roughness, and chemistry. Despite its seeming simplicity, understanding these
48 intriguing liquid-wetting behaviors requires probing the complex solid-liquid interaction that
49 manifests itself as the contact angle [11].

50 Conventionally, the Young contact angle is central to describing a wetting system since it
51 provides the critical boundary condition for the bulk liquid [12,13]. For example, the equilibrium
52 droplet profile on an ideal surface is dictated by the Young contact angle through the Young-
53 Laplace equation

$$54 \quad P_g - P_l = P_c, \quad (1)$$

55 in which P_g and P_l are the pressure in the gas and liquid phase. P_c is the capillary pressure induced
56 by the interface curvature $P_c = \sigma K$. σ is the liquid-gas interface surface tension, and K is the
57 interface curvature. The prediction of Eq. 1 provides a truncated-spherical shape of the droplet
58 profile. On the contrary, experimentally observed nano-scale droplet profiles have always
59 exhibited a meniscus within 20 nm thickness from the contact line even on smooth and
60 homogeneous surfaces [14–16]. This deviates from the prediction based on the Young contact
61 angle. In a recent experimental measurement of the nano-droplet profile, Samoila *et al.* obtained
62 completely different contact angles of the nano-droplets with different volumes on the same
63 surface [17]. This indicates that the Young contact angle as the boundary condition is insufficient
64 to describe the nano-scale wetting phenomena. Therefore, an exact mechanism to explain the
65 deviation can be crucial to numerous nano-scale wetting-related phenomena, *e.g.*, interfacial mass
66 transport [18,19] and contact line dynamics [20,21].

67 To account for this deviation, the effect of the solid-liquid molecular interaction [17,19,22]
68 near the contact line has been investigated extensively. The solid-liquid interaction gives rise to
69 the scale-dependent surface molecular forces and distorts the gas-liquid interface. In addition, the
70 contact angle of a droplet below a critical size has been found dependent on the droplet size
71 [16,23,24], *i.e.*, the line tension effect. Although descriptions of both effects have been well
72 established in the past decades, there seems to exist an internal connection that is still confusing.
73 Indeed, surface molecular forces can strongly influence the interface curvature [25]. On the other
74 hand, the line tension, as a manifestation of surface molecular forces near the contact line, is
75 dependent on the curvature of the gas-liquid interface [26,27]. Interestingly, a recent molecular

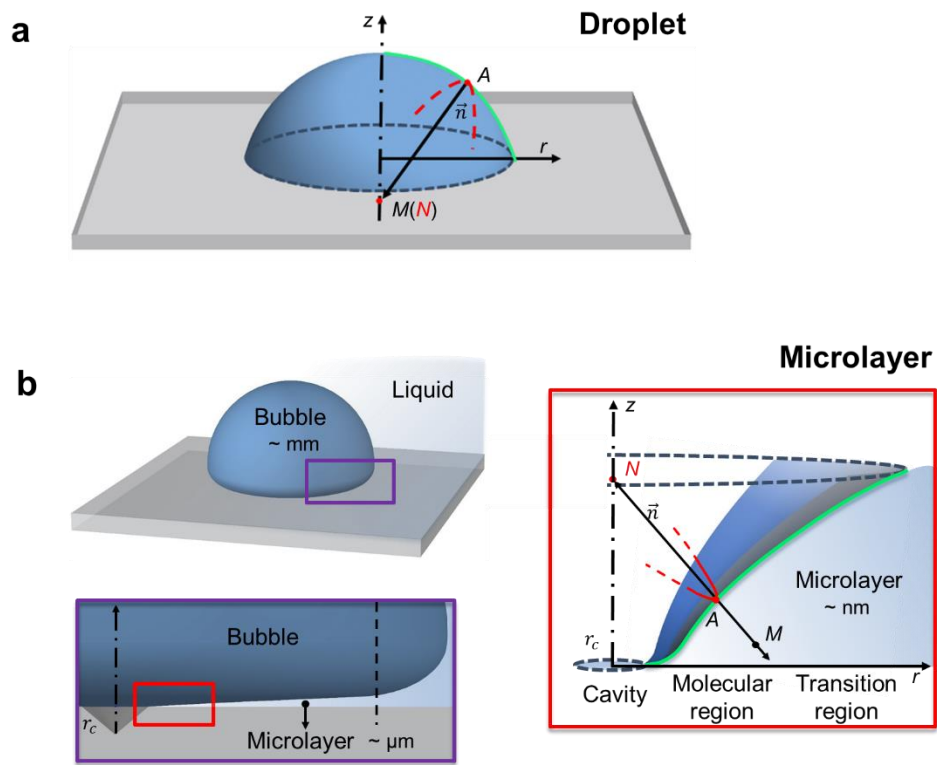
76 dynamics (MD) simulation suggested that the effect of gas-liquid interface curvature and the effect
77 of surface molecular forces are entangled [28]. This is not surprising given that these two effects
78 have an identical origin, *i.e.*, molecular interactions [29]. However, the entanglement brings
79 difficulties in understanding how a nano-scale droplet profile deviates. An insight into the
80 entangled relationship between the effect of surface molecular forces and the effect of the gas-
81 liquid interface curvature is needed.

82 The interface curvature of a 3D axisymmetric droplet is characterized by two principal
83 curvatures κ_1, κ_2 as $K = \kappa_1 + \kappa_2 = \frac{\delta''}{(1+\delta'^2)^{\frac{3}{2}}} + \frac{\delta'}{r(1+\delta'^2)^{\frac{1}{2}}}$ (**Fig. 1a**). δ represents the height of the
84 droplet profile, and r is the radius. However, the principal curvatures of a droplet have the same
85 signs: $\kappa_1\kappa_2 > 0$, that is, the capillary pressure caused by both principal curvatures increases the
86 liquid pressure and promotes the formation of a spherical droplet. In this case, the deviation of an
87 actual droplet profile only occurs at the microscopic scale, thus veiling the physics of the entangled
88 effect.

89 An interesting case of a surface wetting configuration with principal curvatures of different
90 signs is the microlayer in the inertia-controlled bubble growth stage in nucleate boiling, which is
91 a μ -meter thin liquid film trapped underneath a rapidly growing bubble. Besides being of practical
92 importance for heat transfer applications [30–32], the microlayer is a good example to illustrate
93 the entangled effect of the contact line geometry and surface molecular forces. Unlike the spherical
94 droplet (**Fig. 1a**), the 3D profile of the microlayer is saddle-shaped (**Fig. 1b**) and $\kappa_1\kappa_2 < 0$. In this
95 case, the capillary pressure induced by interface curvatures can be understood to both increase and
96 decrease the liquid pressure, depending on the direction of the principal curvature.

97 The accurate description of the microlayer has been a challenge for decades. Previous works
98 mainly resort to DNS simulations and mechanistic models to tackle the hydrodynamic part of this
99 problem [31,33–35], which failed to explain the very thin microlayer obtained in recent
100 experiments [36–38]. It is also worthy mentioning that some recent microlayer simulations have
101 achieved comparable thickness with the experiment results by considering the effects of
102 microlayer evaporation [39–41] and contact line dewetting [42,43]. Nevertheless, the obvious
103 microlayer evaporation and the contact line dewetting were observed only after the early stage
104 [36,44,45], referred to as the diffusion-controlled bubble growth stage [46].

105 This work aims to reveal how the effect of surface molecular forces and the effect of the gas-
 106 liquid interface curvature are entangled. We first studied the entangled effects on the deviation of
 107 a 3D nano-droplet profile by using MD simulations. Then we developed a three-region description
 108 of the microlayer (**Fig. 1b**) that considers the entangled effects of surface molecular forces and
 109 gas-liquid interface curvature. We elucidated the relationship between the effect of surface
 110 molecular forces and the effect of the gas-liquid interface curvature. We found that the mechanism
 111 responsible for the deviation of a nano-droplet profile can explain the very thin microlayer, though
 112 the detailed manifestations of the entanglement are different in the context of the nano-droplet and
 113 microlayer.



114
 115 **Fig. 1. Geometry configurations of surface wetting examples.** (a) Schematic of a 3D droplet
 116 on a solid surface. \vec{AM} and \vec{AN} are the radii of the principal curvatures κ_1 and κ_2 of the gas-liquid
 117 interface (Green line). (b) Schematic of a 3D multiscale microlayer underneath a growing bubble
 118 in the inertia-controlled bubble growth stage in nucleate boiling. The microlayer consists of a
 119 molecular region, a transition region, and a hydrodynamic region. The molecular region starts from
 120 the edge of a cavity, followed by the transition region and the hydrodynamic region of the

121 microlayer. r_c is the radius of the cavity. \overline{AM} and \overline{AN} are the radii of the principal curvatures κ_1
122 and κ_2 of the microlayer vapor-liquid interface (Green line).

123 **2. Methods**

124 *2.1 Molecular dynamics simulation*

125 The equilibrium 3D nano-droplets on silicon (1 0 0) substrate are simulated to investigate the
126 entangled effect of surface molecular forces and the interface curvature by using MD simulations
127 via the LAMMPS software package [47]. Specifically, we vary the footprint radii of the droplet (5
128 nm, 7.5 nm, and 10 nm) to account for the effect of the interface curvature. The surface molecular
129 forces between water molecules and silicon atoms are modeled by the 12-6 L-J potential via silicon
130 and oxygen atoms with the parameters $\sigma_{\text{Si-O}} = 3.41 \text{ \AA}$ and $\varepsilon_{\text{Si-O}} = 1.457 \text{ KJ/mol}$ [48]. The water
131 is modeled by the SPC/E model. The interaction between oxygen and hydrogen atoms is modeled
132 by the long-range Coulombic potential. The cutoff distance for LJ potential is set as 15 \AA . The
133 water molecules are initialized at 1 K in a rectangular box away from the surface and then the
134 temperature is increased to 300 K with an increment of 50 K. Each temperature increment phase
135 is 50 ps. The temperature is maintained at 300 K for another 250 ps to reach equilibrium. The
136 droplet is then brought to the substrate within 3 Angstrom. The spreading and equilibration of the
137 droplet on the surface are for 3 ns. The entire simulation is carried out in the canonical (NVT)
138 ensembles at 300 K using a Nosé-Hoover thermostat. To obtain the statistical droplet profile, we
139 record the positions of water molecules with 1 ps interval in the final 0.2 ns.

140 *2.2 Liquid-gas interface shape model*

141 We employ the augmented Young-Laplace equation to account for the entangled effect of
142 surface molecular forces and gas-liquid interface curvature, given as

$$143 \quad P_g - P_l = P_c + P_d, \quad (2)$$

144 where P_d is the disjoining pressure, originating from the surface molecular forces acting on the
145 liquid phase in the equilibrium state [49]. The augmented Young-Laplace equation coupled with
146 various disjoining pressure has been applied in numerous microscopic liquid droplet/film problems
147 [17,50,51]. However, the entangled effect has never been recognized. The main reason is that
148 liquid with infinite size was considered in most cases. In Eq. 2, we consider the entangled effect

149 as a sum of the capillary pressure and the disjoining pressure to determine the liquid-gas interface
150 shape. According to the extended DLVO theory, the disjoining pressure, P_d , mainly includes four
151 components $P_d = P_{vdW} + P_{st} + P_{ha} + P_{dl}$ [25,52,53], where P_{vdW} is the van der Waals force, P_{st}
152 is steric repulsion, P_{ha} is hydrophobic attraction force, P_{ha} is the electrostatic double-layer force.
153 These four components can cover non-covalent interactions, such as for a silicon-water-vapor
154 system [53].

155 Van der Waals force is expressed as $P_{vdW} = -\frac{A}{\delta^3}$ [25,53]. A is the Hamaker constant, which
156 is related to the solid-liquid van der Waals interaction energy by $A = 12\pi\Delta G^{LW}d_0$. ΔG^{LW} is the
157 solid-liquid Lifshitz–van der Waals interaction free energy, d_0 is the minimum equilibrium
158 distance between two condensed-phase surfaces and is considered a constant of 0.157 nm [53].
159 The steric repulsion arises at very small distances to the adsorbed film on a surface. A commonly-
160 used expression of steric repulsion is given by $P_{st} = -\frac{B}{\delta_0^9}$. B equals to $6A\delta_0^6$ [25]. δ_0 is the
161 thickness of the adsorbed thin film on a given surface. The hydrophobic attraction force can
162 originate when the water molecules near surfaces are induced to order into layers with orientation
163 structure. There is still no universal law for hydrophobic attraction. Here we adopt the expression
164 as $P_{ha} = \Delta G^{AB}e^{-\delta/\lambda} + \Delta G_d^{AB}e^{-\delta/\lambda_d}$ [52,54]. The first term is the short-range hydrophobic force,
165 ΔG^{AB} is the liquid-solid polar interactive free energy. λ is the water characteristic decay length
166 and has to be obtained from experiments. The second term represents the long-range hydrophobic
167 force, whereby ΔG_d^{AB} is considered 1000 times less than ΔG^{AB} according to the previous force
168 measurements [55]. λ_d is by one order of magnitude larger than λ [54]. Electrostatic double-layer
169 force can play a strong role in long-range interactions between electrolytes and a solid surface
170 [56]. However, it exists only between charged molecules (ions) or surfaces and depend on the
171 electrolyte concentration [57]. We examined the contribution of the electrostatic double-layer
172 force to the overall surface molecular forces and found that the electrostatic double-layer force is
173 much weaker compared to other components for the deionized water (A detailed description can
174 be found in the **Supporting Information**). Therefore, we only consider three types of the surface
175 molecular forces, i.e., $P_d = P_{vdW} + P_{st} + P_{ha}$. Note that the disjoining pressure reduces the liquid
176 pressure when it is repulsive.

177 The considered surface molecular forces are defined in terms of solid-liquid-gas interaction
 178 free energy ΔG_{slv} . Based on the Dupré equation $\Delta G_{slv} = \gamma_{sl} - \gamma_{sg} - \gamma_{lg}$, we can express the
 179 disjoining pressure P_d by interfacial energy γ_{sl} , γ_{sg} , and γ_{lg} . Then, the interfacial energy γ_{sl} can
 180 be further related to the surface energy γ_s and γ_l based on the multi-component approach by Oss
 181 $\gamma_{sl} = (\sqrt{\gamma_s^{LW}} - \sqrt{\gamma_l^{LW}})^2 + 2(\sqrt{\gamma_s^+} - \sqrt{\gamma_l^+})(\sqrt{\gamma_s^-} - \sqrt{\gamma_l^-})$ [58], where γ_s^{LW} , γ_s^+ and γ_s^- are the
 182 Lifshitz–van der Waals surface energy and the polar Lewis acid-base surface energy. Note γ_g is
 183 zero in this work. Therefore, the disjoining pressure for a fixed wetting liquid is determined by the
 184 surface energy, which can be obtained by measuring the contact angle of three different liquids on
 185 the surface. The expression of the disjoining pressure and the derived relationship between
 186 interaction free energy and surface energy are summarized in **Table 1**. For the sake of simplicity,
 187 we shall name the above-mentioned augmented Young-Laplace equation coupled with the multi-
 188 component approach as the **M model**. The calculation methods for the M model can be found in
 189 the **Supporting Materials**.

190 The M model provides us with a general mathematical formula to describe the liquid-gas
 191 interface profile on any given surface. To validate the M model, we compare the predicted profile
 192 by the M model with the MD simulated profile. As shown in **Fig. 2**, a good agreement indicates
 193 the validity of the M model for the considered case. Note that the M model cannot capture the
 194 details of the droplet profile on the sub-nanoscale. It is because the actual footprint radii of the
 195 nano-droplet in MD simulation are difficult to determine when we consider Diaz’s approach,
 196 which considers a zero slope of the profile at the contact line [59].

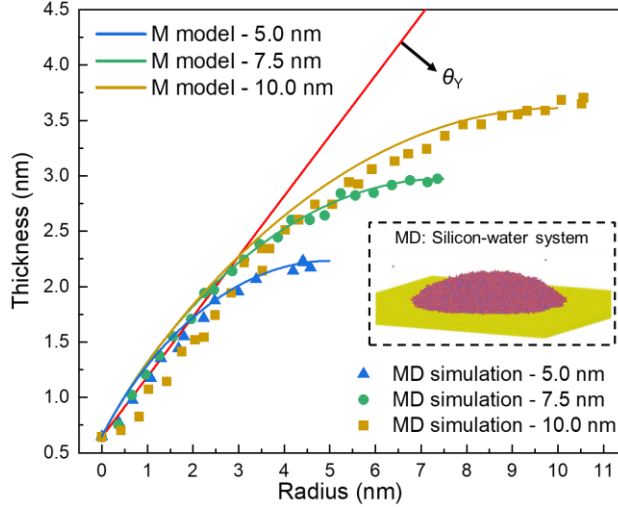
197 **Table 1. Components of the M model: disjoining pressure and its relationship with surface**
 198 **energy**

Van der Waals force P_{vdW}	$P_{vdW} = -\frac{A}{\delta^3} [25];$ <p>A: Hamaker constant, $A = 12\pi\Delta G^{LW}d_0;$</p> <p>$\Delta G^{LW}$: liquid-solid Lifshitz-van der Waals interaction free energy;</p>
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	<p>d_0 : minimum equilibrium distance between two condensed phase surfaces = 0.157 nm [53]</p>
Steric repulsion P_{st}	<p>$P_{st} = -\frac{B}{\delta^9}$ [25];</p> <p>$B = 6A\delta_0^6$; δ_0 : thickness of the adsorbed thin film on a given surface</p>
Hydrophobic attraction force P_{ha}	<p>$P_{ha} = \Delta G^{AB} e^{-\delta/\lambda} + \Delta G_d^{AB} e^{-\delta/\lambda_d}$ [52,54]</p> <p>ΔG^{AB} : liquid-solid polar interaction free energy;</p> <p>λ: water characteristic decay length;</p> <p>$\Delta G_d^{AB} = \Delta G^{AB}/1000$ [55], $\lambda_d > 10\lambda$[54]</p> <p>$\Delta G^{AB} e^{-\delta/\lambda}$: short-range hydrophobic force</p> <p>$\Delta G_d^{AB} e^{-\delta/\lambda_d}$: long-range hydrophobic force</p>
Lifshitz-van der Waals interaction free energy ΔG^{LW}	<p>$\Delta G^{LW} = 2[\sqrt{\gamma_s^{LW}\gamma_l^{LW}} + \sqrt{\gamma_g^{LW}\gamma_l^{LW}} - \sqrt{\gamma_s^{LW}\gamma_g^{LW}} - \gamma_l^{LW}]$ [58], γ^{LW}: Lifshitz-van der Waals surface energy</p>
Polar interaction free energy ΔG^{AB}	<p>$\Delta G^{AB} = 2[\sqrt{\gamma_l^+}(\sqrt{\gamma_s^-} + \sqrt{\gamma_g^+} - \sqrt{\gamma_l^-}) - \sqrt{\gamma_l^-}(\sqrt{\gamma_s^+} + \sqrt{\gamma_g^-} - \sqrt{\gamma_v^+}) - \sqrt{\gamma_s^+\gamma_g^-} - \sqrt{\gamma_s^-\gamma_g^+}]$ [58], γ^+ and γ^- : the polar Lewis acid-base surface energy</p>

199

200



201
 202 **Fig. 2.** Comparison of the droplet profiles on the nano-scale obtained from the M model and MD
 203 simulation simulations. θ_Y is the Young contact angle of a droplet on a silicon surface [60].

204 **3. Results and discussions**

205 *3.1. Deviation of a 3D nano-droplet profile and interface nano-bending*

206 We first start with the deviation of the nano-droplet profile. **Fig. 3a** shows the comparison
 207 between the microscopic droplet profile measured on hydroxylated glass in a recent experiment
 208 and a spherical shape profile [17]. The spherical shape profile is obtained by fitting the upper part
 209 of the droplet profile from the experiment. The microscopic droplet profile shows a deviation from
 210 the spherical shape near the contact line within the distance of several nanometers from the surface.
 211 This deviation was attributed only to the surface molecular forces [17,20]. **Fig. 3b** gives the sub-
 212 nano scale droplet profiles with different footprint radii by using MD simulation. The simulated
 213 droplet profiles also exhibit deviation from the spherical shape profile. In this case, the deviation
 214 is caused by the entangled effect of surface molecular forces and interface curvature. An interface
 215 nano-bending, which shows a concaving pattern on the sub-nanoscale (**Fig. 3b**) and a convex
 216 pattern on the nano-scale (**Fig. 2**), is formed near the contact line. This is similar to the
 217 experimental measurement as shown in **Fig. 3a**.

218 To investigate the relationship between the effect of surface molecular forces and the effect of
 219 the interface curvature, we compare the droplet profiles obtained by MD simulations and
 220 predictions by using Eq. 1 with the boundary condition of the Young contact angle on a silicon
 221 surface. From a mechanical perspective, the Young contact angle is defined at an inflection point

222 on the interface of a droplet with infinite size (2D) where the droplet profile transits from concave
223 to convex in the transition region [59]. In the region with a concave profile, surface molecular
224 forces dominate the droplet profile, while in the region with a convex profile, the hydrodynamic
225 effect dominates. Therefore, the Young contact angle can be understood as a manifestation of
226 surface molecular forces near the contact line. The prediction by Eq. 1 for the finite-size droplet
227 (3D) can be interpreted as a linear superposition of the effect of the surface molecular forces and
228 the effect of the local interface curvature on the interface. This method is pure hydrodynamics and
229 has been widely adopted to calculate the droplet or liquid film profile [61,62]. In **Fig. 3b**, the red
230 line represents the profile with infinite droplet size, and dashed lines give the predictions by Eq. 1
231 with the corresponding footprint radii of MD simulations. With the decrease of the footprint radii,
232 the profiles deviate more from the red line because the capillary pressure induced by the larger
233 curvature distorts the interface.

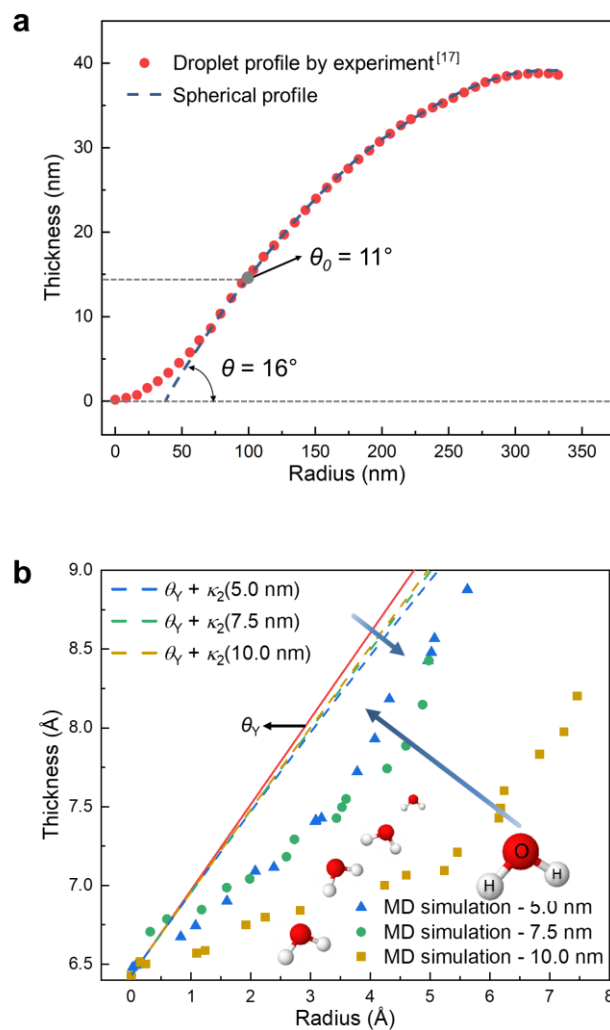
234 However, the droplet profiles by MD simulations deviate more from the red line with the
235 increased footprint radii, which is in contrast to the calculated profiles by Eq. 1. This unexpected
236 result implies the effect of surface molecular forces and the effect of the interface curvature on a
237 3D nano-droplet profile are nonlinearly coupled. In other words, any distortion of the droplet
238 profile caused by one effect simultaneously influences the other one. Thus the interface nano-
239 bending can be understood as a manifestation of the nonlinear-coupled effect near the contact line.
240 The nonlinear-coupled effect may also be influenced by surface heterogeneities and external force
241 fields that can further deform the interface. Therefore, the nonlinear-coupled effect is universal
242 and demands consideration when modeling wetting phenomena.

243 *3.2. Nonlinear-coupled effect*

244 To understand the nonlinear-coupled effect, one must go through the manifestation of surface
245 molecular forces in the interface nano-bending. For example, the 12-6 L-J intermolecular pair
246 potential used in the MD simulation gives rise to surface molecular forces between the liquid-gas
247 interface and the solid-liquid interface [52]. The gas-liquid interface experiences first repulsive
248 force near the surface, and then attractive force when the interface is away from the surface. This
249 qualitative description of the surface molecular forces explains the 3D droplet profile (**Fig. 3b**)
250 obtained by MD simulation very well. However, to answer why the droplet profile deviates more
251 from the red line with the increase of the footprint radii, we need to analyze the role of the interface

252 curvature. Considering an equilibrium droplet, the liquid pressure inside the droplet is uniform.
 253 According to Eq. 1, the droplet profile dominated by capillary pressure is convex and with smaller
 254 curvature when the footprint radii are larger. Therefore, the role of surface molecular forces and
 255 the interface curvature act in opposite ways within the range of repulsive surface molecular forces,
 256 while they both act to formulate a convex interface within the range of attractive surface molecular
 257 forces. As a result, the droplet profile on the sub-nanoscale deviates more with the increase of the
 258 footprint radii. A quantitative description of the nonlinear-coupled effect will rely on the analysis
 259 of the microlayer model in the next sections.

260



261

262 **Fig. 3. Deviation of the 3D nano-droplet profile.** (a) Comparison of the nano-droplet profile
 263 obtained from the experiment and a spherical shape. θ_0 is the contact angle at the inflection point
 264 obtained from the experiment [17]. θ is the contact angle obtained from the spherical shape profile.

265 (b) Comparison of the droplet profiles on the sub-nanoscale obtained from the MD simulations
266 and Eq. 1. θ_Y is the Young contact angle of a droplet on a silicon surface, κ_2 is the principal
267 curvature of the interface that is related to the droplet footprint radii.

268 3.3. Profile of the microlayer in the inertia-controlled bubble growth stage

269 We model the microlayer profile in the inertia-controlled stage in nucleate boiling, also
270 referred to as the initial stage [33]. The concept of the inertia-controlled stage was first proposed
271 in a seminal paper by Mikic *et al.* [46]. In this stage, the bubble expands at a constant speed fueled
272 by the overpressure of the vapor because its high internal pressure prevents the evaporation from
273 the surrounding liquid under low superheat. In the last decade, the snapshots of the microlayer
274 profile from several experiments using the laser interferometry method show that the formed
275 microlayer profile remains almost stationary within a very short time (~ 0.6 ms) after the bubble
276 nucleation [36,44]. This confirms ignorable evaporation from the microlayer at the beginning of
277 the microlayer formation, namely, the inertia-controlled stage. Besides, the extrapolation of the
278 microlayer profile indicates that there is no contact line movement, thus we can assume a no-slip
279 boundary condition. The stationary microlayer allows us to avoid a transient microlayer in the
280 inertia-controlled stage. As also shown in the literature [31], the interface of the microlayer evolves
281 along with a fixed profile. In this work, we focus on the inertia-controlled stage, thus only the
282 nonlinear-coupled effect and the hydrodynamic effect are considered in modeling the microlayer.

283 The nonlinear-coupled effect and the hydrodynamic effect are considered separately. We
284 divide the microlayer into three regions (**Fig. 1b**): a molecular region, a transition region, and a
285 hydrodynamic region. The nonlinear-coupled effect is accounted for in the molecular and
286 transition region. The interface shape in these two regions can be described by Eq. 2. When a
287 hemispherical bubble nucleus is trapped in a cavity with the radius r_c , the required superheat to
288 activate the nucleate boiling is related to r_c [46]. In this work, we use $r_c = 2.8 \mu\text{m}$, for which the
289 corresponding activation superheat is 12 K. In the transition region, surface molecular forces
290 become less significant compared to the capillary pressure, thus we assume that the transition
291 region ends when the capillary pressure is much larger (*e.g.*, 10 times) than surface molecular
292 forces. The required two initial conditions at the contact line are given as $\delta_0 = 0.157 \text{ nm}$ [53] and

293 $\delta'_0 = 0$, representing the adsorbed film thickness and the initial slope of the film profile.
 294 Parameters regarding the surface energy used in the M model are listed in **Table 2**.

295 **Table 2. Surface energy components of studied surfaces.**

Surface	γ^{LW} (mJ/m ²)	γ^+ (mJ/m ²)	γ^- (mJ/m ²)	Young CA (degree)	λ [54] (mm)
Glass[63]	38.2	1.2	49	23.80	0.4459
Silicon[60]	38.6	4	33.98	28.14	0.4613
ITO[64]	45.8	0	63.8	12.60	0.3434
Silica[65]	39.0	0.6	56	18.90	0.3871
Weakly hydrophilic	38.6	4	1.9	75.08	1.1256

296 **Fig. 4a** shows the microlayer profiles in the molecular and transition region on glass, silica,
 297 ITO, and silicon surfaces, all of which are calculated by the M model. These profiles vary in
 298 thickness due to the different surface energy. Nevertheless, we observe a fixed pattern of the
 299 profiles on each surface. The profile first exhibits a concaving pattern and then transits to convex
 300 with the slope starting to decrease continuously. This is because, within the nano-scale thickness
 301 of the microlayer, the repulsive and attractive molecular forces are dominant in turn. Together with
 302 the capillary pressure, a strong interface nano-bending presents within several nanometers of
 303 thickness, leading to a significant reduction of both profile thickness and slope in the molecular
 304 region. Such a nano-bending, analogy to that in the nano-droplet case, is a manifestation of the
 305 nonlinear-coupled effect between surface molecular forces and interface curvature. With the
 306 increase of the microlayer thickness, surface molecular forces decay rapidly and the capillary
 307 pressure becomes dominant, whereas the bending of the profiles becomes less significant,
 308 indicating the start of the hydrodynamic region.

309 For the hydrodynamic region of the microlayer, the hydrodynamic effect is dominant. Since
 310 the microlayer is very thin, we apply a lubrication approximation in cylindrical coordinates to
 311 describe the liquid flow in the microlayer. Here we derive an **H model** based on Nikolayev's
 312 approach [66], given as

313
$$\frac{\partial}{\partial r} \left[\delta \left(\frac{\delta}{2} + l_s \right) \frac{\partial \sigma}{\partial r} + \delta^2 \left(\frac{\delta}{3} + l_s \right) \frac{\partial P_c}{\partial r} \right] = \mu \left(u^i - \frac{J}{\rho_L} \right). \quad (3)$$

314 l_s is the slip length of the liquid-solid interface, which is not considered in the microlayer in the
 315 inertia-controlled stage. u^i is the normal interface velocity and is considered to be positive if
 316 directed inside the liquid, $\frac{\partial \sigma}{\partial r}$ represents the Marangoni effect, and J is the mass evaporation flux
 317 at the interface. Considering the stationary microlayer profile [36] and nearly homogenous
 318 distributed temperature along the microlayer interface, u^i , $\frac{\partial \sigma}{\partial r}$, and J can be eliminated. Substitute
 319 the expression of the capillary pressure P_c into Eq. 3, the governing equation becomes

320
$$\frac{\partial}{\partial r} \left[\frac{\delta^3}{3} \frac{\partial}{\partial r} \left(\frac{\delta''}{(1+\delta'^2)^{\frac{3}{2}}} + \frac{\delta'}{r(1+\delta'^2)^{\frac{1}{2}}} \right) \sigma \right] = 0. \quad (4)$$

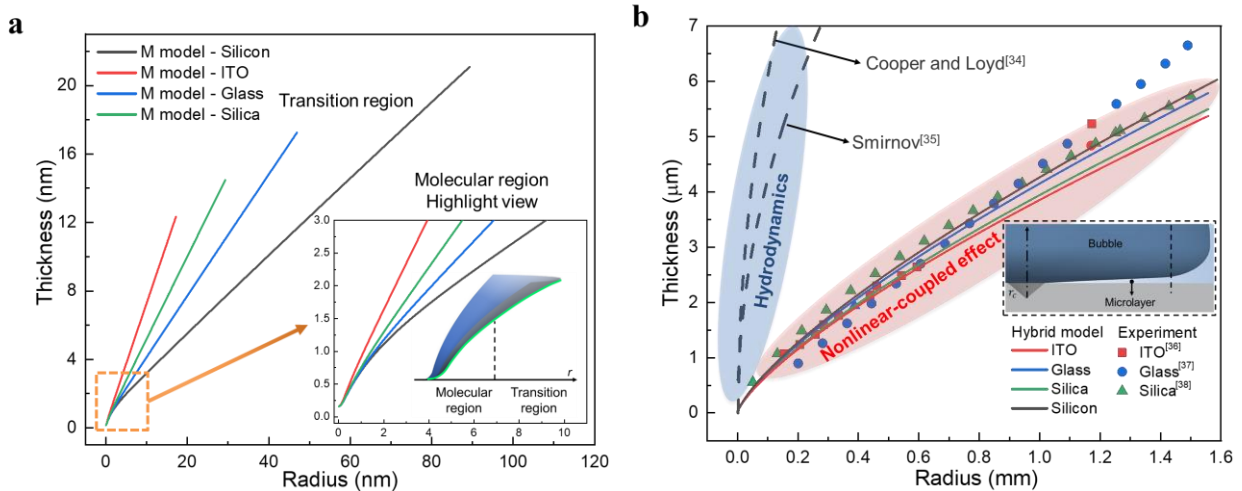
321 **Fig. 4a** shows that the slope variation in the transition region is much weaker compared to that
 322 in the molecular region. Further, the experimental microlayer profiles [36,44,67] are
 323 approximately linear over the micron scale. This indicates the slope variation of the microlayer
 324 profile in the hydrodynamic region is very limited. Thus, we integrate Eq. 4 with respect to r and
 325 neglect the terms with second and third-order derivatives of δ . Then an analytical solution of Eq.
 326 4 can be easily derived as

327
$$\delta = \sqrt[4]{C_1 r^3 + C_2}, \quad (5)$$

328 with $C_1 = -\frac{4C}{\sigma}$, $C_2 = \delta_a^4 + \frac{4C}{\sigma} r_a^3$, and $C = -\frac{\delta'_a \delta_a^3 \sigma}{3r_a^2}$. C , C_1 , and C_2 are the constants of integration.
 329 The subscript a represents an arbitrary position along the microlayer in the hydrodynamic region.
 330 Eq. 5 gives the microlayer profile in the hydrodynamic region. The derivation of the analytical
 331 solution Eq. 5 is included in the **Supporting Materials**.

332 According to Eq. 5, the microlayer thickness δ and the interface slope δ' at an arbitrary position
 333 along the microlayer are required to determine the constants C , C_1 , and C_2 . Here we develop a
 334 **hybrid model** that covers both the M model and H model by approximately matching the transition
 335 region and the hydrodynamic region. In other words, the molecular region and the transition region

336 are considered the inner boundary for the entire microlayer. We use the calculated results at the
 337 out end of the transition region by the M model to determine the constants of integration (see **Table**
 338 **S1** in the **Supporting Materials**). For surfaces of glass, silica, ITO, and silicon, C_1 has very close
 339 value, this indicates that the slopes of the microlayer profiles are similar on these surfaces.
 340 Furthermore, the calculated C_2 is much smaller than C_1 , thus C_2 can be ignored given the
 341 millimeter-length microlayer. Now Eq. 5 reduces to $\delta = \sqrt[4]{C_1}r^{0.75}$. It has a similar form to
 342 Yabuki's expression $\delta = 5.10 \times 10^{-4}r^{0.69}$, which was obtained by fitting their experimental data
 343 [38]. **Fig. 4b** displays the microlayer profiles predicted by our hybrid model and the comparison
 344 with previous models and experiments [36–38]. The well-known models derived by Cooper and
 345 Smirnov follow from different hydrodynamic descriptions yet both relate the microlayer thickness
 346 to the bubble growth time [34,35], expressed as $\delta = C\sqrt{\nu t_g}$. The bubble growth time t_g can be
 347 related to the bubble growth speed. The constant C is obtained from an experimental fit and is
 348 proportional to the bubble growth speed. As shown in **Fig. 4b**, the results largely overestimate the
 349 microlayer thickness, that is, the hydrodynamic effect cannot “bend down” the microlayer
 350 effectively. The hybrid model successfully predicts the microlayer profile by considering a new
 351 inner boundary condition, which is derived based on the nonlinear-coupled effect.



352

353 **Fig. 4. Multiscale microlayer profile on various surfaces.** (a) Microlayer profiles from the
 354 molecular region to the transition region on various surfaces predicted by the M model. (b) Full
 355 picture of the predicted microlayer profiles by the hybrid model and the comparison with previous

356 models and experiment data. Microlayer profile predictions in the blue region and red region are
357 based on the hydrodynamics and non-linear coupled effect, respectively.

358 *3.4. Deviation of the microlayer profile*

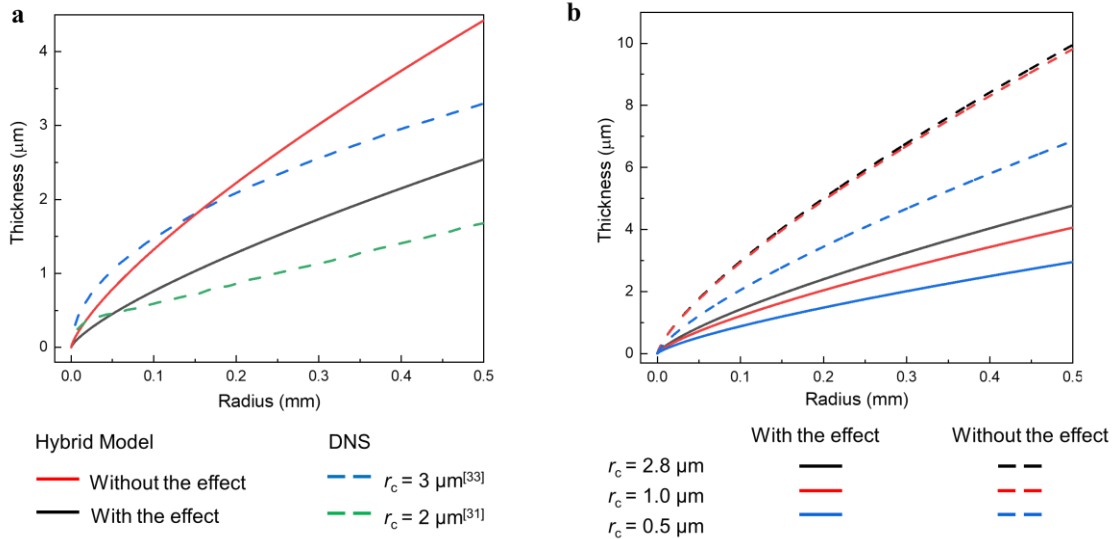
359 To understand how the nonlinear-coupled effect formulates the inner boundary condition for
360 the microlayer, we revisit the interface nano-bending in the molecular region (see **Fig. 4a** highlight
361 view). The repulsive surface molecular forces first raise the interface, and consequently, the effect
362 of the second principal curvature κ_2 is enhanced within the thickness of several angstroms. Note
363 that the capillary pressure induced by the second principal curvature increases the liquid pressure,
364 thus preventing the rise of the profile. With the increase in thickness, surface molecular forces turn
365 attractive. Together with the second principal curvature, both act to bend the profile downward.
366 The second principal curvature retards the decay of surface molecular forces and therefore
367 contributes to a further bending of the microlayer profile. The role of the nonlinear-coupled effect
368 differs from that in the nano-droplet. In the case of the microlayer, the coupling effectively
369 strengthens the role of both surface molecular forces and the interface curvature and becomes more
370 powerful in bending the profile.

371 We further consider a linear superposition of the impacts between surface molecular forces
372 and the interface curvature on the profile by bringing each into effect within two consecutive
373 regions starting from the contact line. In the first region, we only consider surface molecular forces
374 and the first principal curvature. We rewrite Eq. 2 as $P_v - P_l = \kappa_1 + P_d$ to describe the microlayer
375 profile. Similar to the interpretation of the Young contact angle of a 2D droplet [59], the Young
376 contact angle is formed in the first region. In the second region, the second principal curvature
377 takes effect and surface molecular forces vanish, the microlayer profile can be described as $P_v -$
378 $P_l = (\kappa_1 + \kappa_2)\sigma$. The boundary between these two regions is where the Young contact angle starts
379 to form in the first region, and the outer end of these two regions is considered to reach the same
380 slope as that at the outer end of the transition region in **Fig. 4a**. In this case, effects of the surface
381 molecular forces and the second principal curvature are linearly superposed, as we discussed in
382 the interpretation of Eq. 1. The calculated results are used to determine C_1 and C_2 in Eq. 5. We
383 show the microlayer profile with and without considering the nonlinear-coupled effect in **Fig. 5a**.
384 The microlayer thickness without the nonlinear-coupled effect reaches around $4.5 \mu\text{m}$ at 0.5 mm
385 microlayer length, almost 2 times higher than that with the nonlinear-coupled effect.

386 Next, we compare the predicted microlayer profiles with DNS simulations to elucidate the
 387 critical role of the inner boundary condition. As shown in **Fig. 5a**, the microlayer profile obtained
 388 by Guion *et al.* has a larger thickness [33]. On the other hand, the thickness of the microlayer
 389 profile in Ding’s work is smaller [31] as there a smaller bubble nucleus size of 2 μm has been
 390 assumed compared to the 3 μm in Guion’s work. It directly shows the significance of the bubble
 391 nucleus size. As indicated by the curvature expression $K = \frac{\delta''}{(1+\delta'^2)^{\frac{3}{2}}} + \frac{\delta'}{r(1+\delta'^2)^{\frac{1}{2}}}$, the capillary
 392 pressure induced by the second principal curvature would be extremely large with the smaller
 393 bubble nucleus. Such large capillary pressure can effectively “bend down” the microlayer. In the
 394 DNS simulation, the Young contact angle is imposed as the boundary condition, while in our
 395 hybrid model, δ'' is also included in the boundary condition and determines the entire microlayer
 396 profile implicitly through Eq. 4. The new boundary condition derived based on the nonlinear-
 397 coupled effect can be considered as a local pressure boundary condition, which is formulated by
 398 the sum of the interface curvature induced capillary pressure and the disjoining pressure in the
 399 molecular and transition region. From a perspective of the molecular force, the role of the
 400 nonlinear-coupled effect on the macroscale microlayer can be understood as that molecular forces
 401 by both water and surface are superimposed on the water-vapor interface in the molecular region
 402 and transmitted to the macroscale. In other words, the microlayer profile is a macroscale
 403 manifestation of the interaction between the solid surface and water molecules. Nevertheless,
 404 numerous previous works have also attempted to incorporate the augmented Young-Laplace
 405 equation in the DNS simulation of the microlayer.[41,68–71] Though as we discussed, the
 406 augmented Young-Laplace can account for the nonlinear-coupled effect, to the best of our
 407 knowledge, there is still no related report of the successful prediction of the microlayer profile.
 408 The most important reason is that a rather larger bubble nucleus was employed in these
 409 simulations, which overlooked the effect of the interface curvature.

410 Finally, we discuss the microlayer profile on a weakly hydrophilic surface. As shown in **Fig.**
 411 **5b**, on a surface with the Young contact angle of 75.08° the microlayer thickness predicted by the
 412 hybrid model increases to $\sim 10 \mu\text{m}$ at 0.5 mm length. Nevertheless, the required cavity radius (*i.e.*,
 413 nucleus size) to activate the nucleation is influenced by surface wettability. Previous studies based
 414 on thermodynamic analyses suggested a negative correlation between the critical cavity radius and
 415 surface wettability [72,73]. Thus, we assume a reduction of the cavity radius r_c on a weakly

416 hydrophilic surface. The results for $r_c = 2.8, 1.0, 0.5 \mu\text{m}$ are plotted in **Fig. 5b**. When r_c decreases
 417 the thickness of the microlayer profile decreases too and the actual microlayer profile is met for
 418 $r_c = 0.5 \mu\text{m}$. In addition, we can see a stronger impact of the nonlinear-coupled effect on weakly
 419 hydrophilic surfaces, because the radii of the second principal curvature are much smaller when
 420 the slope of the profile is larger.



421
 422 **Fig. 5. Deviation of the microlayer profile.** (a) Impact of the nonlinear-coupled effect on
 423 microlayer profile and comparison with DNS simulations. The green dashed line is from the
 424 simulation of Guion *et al.*; the blue dashed line is from the simulation of Ding *et al.* (b) Microlayer
 425 profile on the weakly hydrophilic surface with and without the nonlinear-coupled effect (Young
 426 contact angle = 75.08°).

427 4. Conclusions

428 In this work, we revealed a nonlinear-coupled effect between the liquid-gas interface geometry
 429 and the solid-liquid interactions in the microscopic liquid-wetting phenomenon. We performed
 430 MD simulations for nano-droplets to examine the nonlinear-coupled effect. Then we applied it in
 431 the multiscale modeling (M-Model, H-Model, and hybrid model) of a microlayer in the inertia-
 432 controlled bubble growth stage in nucleate boiling. The hybrid model successfully predicted the
 433 microlayer profile captured by different experiments [36–38] for the first time. We found that the
 434 nonlinear-coupled effect is responsible for the deviation of a nano-droplet profile from the
 435 prediction based on the conventional Young contact angle. Furthermore, the very thin microlayer

436 thickness in the inertia-controlled bubble growth stage is determined by the nonlinear-coupled
437 effect, instead of the hydrodynamic effects considered in recent DNS simulation works [33,42,43].

438 The nonlinear-coupled effect explains the mechanism of the microscopic liquid-gas interface
439 deviation from the prediction based on the conventional Young contact angle. We may therefore
440 resolve the long-standing disputes over the validity of the Young contact angle at the nano-scale
441 [28,74,75]. However, the detailed manifestations of the nonlinear-coupled effect depend on the
442 liquid-gas geometries. In the context of the nano-droplet with the principal curvatures of the same
443 signs (spherical shape), the impacts of the interface curvature and the solid-liquid interactions act
444 in the opposite way within the repulsive range of surface molecular forces. In the context of the
445 microlayer with the principal curvatures of the different signs (saddle shape), the nonlinear-
446 coupled effect enhances the impacts of the interface curvature and solid-liquid interactions in
447 bending the microlayer. It indicates that the nonlinear-coupled effect could play a more important
448 role in bubble-related wetting phenomena, such as the long lifetime surface nano-bubble [76].
449 Moreover, the nonlinear-coupled effect structures an interface nano-bending near the surface that
450 can be considered as a new pressure boundary condition for the liquid wetting system. The new
451 pressure boundary condition enables us to unveil mechanisms behind recent intriguing
452 microscopic wetting experiments. For example, the microscopic liquid film evaporation [8], and
453 the surface curvature-driven microscopic droplet motion [6].

454 In future, it would be interesting to reinterpret the line tension based on the nonlinear-coupled
455 effect so that the nonlinear dependency between the cosine of the contact angle of nano-droplets
456 or surface nano-bubbles and the contact line curvature reported in many previous experimental
457 studies [16,77] may be explained.

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461 **CRedit authorship contribution statement**

462 **Jinming Zhang:** Conceptualization, Methodology, Validation, Writing - original draft. **Wei Ding:**
463 Conceptualization, Methodology, Writing - review & editing, Supervision. **Zuankai Wang:**

464 Writing – review & editing. **Hao Wang:** Methodology. **Uwe Hampel:** Conceptualization,
465 Methodology, Writing - review & editing, Supervision. All authors have read and agreed to the
466 published version of the manuscript.

467 **Declaration of Competing Interest**

468 The authors declare that they have no known competing financial interests or personal
469 relationships that could have appeared to influence the work reported in this paper.

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