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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.

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

Liquid wetting on surfaces is ubiquitous in nature and is of great scientific and technological interest [1–4]. Recent examples such as liquid directional steering [5], surface curvature-driven droplet motion [6], ultra-thin water film evaporation [7,8], and triboelectric nanogenerators [9,10] have illustrated the beauty of the wetting phenomena by tailoring the solid surface properties, including curvature, roughness, and chemistry. Despite its seeming simplicity, understanding these
intriguing liquid-wetting behaviors requires probing the complex solid-liquid interaction that
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

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

in which P_g and P_l are the pressure in the gas and liquid phase. P_c is the capillary pressure induced 55 by the interface curvature $P_c = \sigma K$. σ is the liquid-gas interface surface tension, and K is the 56 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 transport [18,19] and contact line dynamics [20,21]. 66

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

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

The interface curvature of a 3D axisymmetric droplet is characterized by two principal curvatures κ_1 , κ_2 as $K = \kappa_1 + \kappa_2 = \frac{\delta''}{(1+\delta'^2)^2} + \frac{\delta'}{r(1+\delta'^2)^2}$ (Fig. 1a). δ represents the height of the droplet profile, and *r* is the radius. However, the principal curvatures of a droplet have the same signs: $\kappa_1 \kappa_2 > 0$, that is, the capillary pressure caused by both principal curvatures increases the liquid pressure and promotes the formation of a spherical droplet. In this case, the deviation of an actual droplet profile only occurs at the microscopic scale, thus veiling the physics of the entangled 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 u-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 droplet (Fig. 1a), the 3D profile of the microlayer is saddle-shaped (Fig. 1b) and $\kappa_1 \kappa_2 < 0$. In this 94 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.

The accurate description of the microlayer has been a challenge for decades. Previous works 97 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 microlayer evaporation [39-41] and contact line dewetting [42,43]. Nevertheless, the obvious 102 103 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.



Fig. 1. Geometry configurations of surface wetting examples. (a) Schematic of a 3D droplet on a solid surface. \overrightarrow{AM} and \overrightarrow{AN} are the radii of the principal curvatures κ_1 and κ_2 of the gas-liquid interface (Green line). (b) Schematic of a 3D multiscale microlayer underneath a growing bubble in the inertia-controlled bubble growth stage in nucleate boiling. The microlayer consists of a molecular region, a transition region, and a hydrodynamic region. The molecular region starts from 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. \overrightarrow{AM} and \overrightarrow{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 and oxygen atoms with the parameters $\sigma_{Si-O} = 3.41$ Å and $\varepsilon_{Si-O} = 1.457$ KJ/mol [48]. The water 130 131 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 Å. 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

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

143
$$P_g - P_l = P_c + P_d,$$
 (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 as a sum of the capillary pressure and the disjoining pressure to determine the liquid-gas interface shape. According to the extended DLVO theory, the disjoining pressure, P_d , mainly includes four 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} is steric repulsion, P_{ha} is hydrophobic attraction force, P_{ha} is the electrostatic double-layer force. These four components can cover non-covalent interactions, such as for a silicon-water-vapor system [53].

Van der Waals force is expressed as $P_{vdW} = -\frac{A}{\delta^3}$ [25,53]. A is the Hamaker constant, which 155 is related to the solid-liquid van der Waals interaction energy by $A = 12\pi\Delta G^{LW} d_0$. ΔG^{LW} is the 156 solid-liquid Lifshitz-van der Waals interaction free energy, d_0 is the minimum equilibrium 157 158 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 commonlyused expression of steric repulsion is given by $P_{st} = -\frac{B}{\delta^9}$. B equals to $6A\delta_0^6$ [25]. δ_0 is the 160 161 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 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, 164 ΔG^{AB} is the liquid-solid polar interactive free energy. λ is the water characteristic decay length 165 166 and has to be obtained from experiments. The second term represents the long-range hydrophobic force, whereby ΔG_d^{AB} is considered 1000 times less than ΔG^{AB} according to the previous force 167 measurements [55]. λ_d is by one order of magnitude larger than λ [54]. Electrostatic double-layer 168 169 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 be further related to the surface energy γ_s and γ_l based on the multi-component approach by Oss 180 $\gamma_{sl} = (\sqrt{\gamma_s^{LW}} - \sqrt{\gamma_l^{LW}})^2 + 2(\sqrt{\gamma_s^+} - \sqrt{\gamma_l^+})(\sqrt{\gamma_s^-} - \sqrt{\gamma_l^-})$ [58], where γ_s^{LW} , γ_s^+ and γ_s^- are the 181 Lifshitz-van der Waals surface energy and the polar Lewis acid-base surface energy. Note γ_q is 182 183 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.

The M model provides us with a general mathematical formula to describe the liquid-gas interface profile on any given surface. To validate the M model, we compare the predicted profile by the M model with the MD simulated profile. As shown in **Fig. 2**, a good agreement indicates the validity of the M model for the considered case. Note that the M model cannot capture the details of the droplet profile on the sub-nanoscale. It is because the actual footprint radii of the nano-droplet in MD simulation are difficult to determine when we consider Diaz's approach, 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 surface198 energy

	$P_{\nu dW} = -\frac{A}{\delta^3} [25];$	
Van der Waals force P_{vdW}	A: Hamaker constant, $A = 12\pi\Delta G^{LW} d_0$;	=
	ΔG^{LW} : liquid-solid Lifshitz-van de Waals interaction free energy;	er

	d_0 : minimum equilibrium distance between two condensed phase surfaces = 0.157 nm [53]
Steric repulsion P_{st}	$P_{st} = -\frac{B}{\delta^9} [25];$ $B = 6A\delta_0^6 ; \delta_0 : \text{ thickness of the}$
	$P_{ha} = \Delta G^{AB} e^{-\delta/\lambda} + \Delta G_d^{AB} e^{-\delta/\lambda_d}$ [52,54]
	ΔG^{AB} : liquid-solid polar interaction free energy;
	λ : water characteristic decay length;
Hydrophobic attraction force P_{ha}	$\Delta G_d^{AB} = \Delta G^{AB} / 1000 [55], \lambda_d > 10$ $\lambda [54]$
	$\Delta G^{AB} e^{-\delta/\lambda}$: short-range hydrophobic force
	$\Delta G_d^{AB} e^{-\delta/\lambda_d}$: long-range hydrophobic force
Lifebitz van der Waals interaction free	$\Delta G^{LW} = 2\left[\sqrt{\gamma_s^{LW}\gamma_l^{LW}} + \sqrt{\gamma_g^{LW}\gamma_l^{LW}} - \right]$
energy ΔG^{LW}	$\sqrt{\gamma_s^{LW} \gamma_g^{LW}} - \gamma_l^{LW}$] [58], γ^{LW} : Lifshitz- van der Waals surface energy
	$A \subset AB \rightarrow C \subset \overline{+} \subset \overline{-+} \subset \overline{+}$
Polar interaction free energy ΔG^{AB}	$\Delta G^{AB} = 2\left[\sqrt{\gamma_l^+} \left(\sqrt{\gamma_s^-} + \sqrt{\gamma_g^+} - \sqrt{\gamma_\nu^+}\right) - \sqrt{\gamma_l^-} \left(\sqrt{\gamma_s^+} + \sqrt{\gamma_g^+} - \sqrt{\gamma_\nu^+}\right) - \sqrt{\gamma_s^+ \gamma_g^-} - \sqrt{\gamma_s^- \gamma_g^+}\right] [58], \ \gamma^+ \text{ and } \gamma^- :$
	the polar Lewis acid-base surface energy

Fig. 2. Comparison of the droplet profiles on the nano-scale obtained from the M model and MD 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.

To investigate the relationship between the effect of surface molecular forces and the effect of the interface curvature, we compare the droplet profiles obtained by MD simulations and predictions by using Eq. 1 with the boundary condition of the Young contact angle on a silicon 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) obtained by MD simulation very well. However, to answer why the droplet profile deviates more 250 251 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

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

(b) Comparison of the droplet profiles on the sub-nanoscale obtained from the MD simulations and Eq. 1. θ_Y is the Young contact angle of a droplet on a silicon surface, κ_2 is the principal curvature of the interface that is related to the droplet foorprint 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 $r_c = 2.8 \ \mu m$, 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 $\delta_0 = 0.157 nm$ [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**.

Secure of	γ^{LW}	γ^+	γ-	Young CA	λ[54]
Surface	(mJ/m^2)	(mJ/m^2)	(mJ/m^2)	(degree)	(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

295 Table 2. Surface energy components of studied surfaces.

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.

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

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

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

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

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

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. The subscript *a* represents an arbitrary position along the microlayer in the hydrodynamic region. Eq. 5 gives the microlayer profile in the hydrodynamic region. The derivation of the analytical solution Eq. 5 is included in the **Supporting Materials**.

According to Eq. 5, the microlayer thickness δ and the interface slope δ at an arbitrary position along the microlayer are required to determine the constants *C*, *C*₁, and *C*₂. Here we develop a **hybrid model** that covers both the M model and H model by approximately matching the transition 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 value, this indicates that the slopes of the microlayer profiles are similar on these surfaces. 339 340 Furthermore, the calculated C_2 is much smaller than C_1 , thus C_2 can be ignored given the millimeter-length microlayer. Now Eq. 5 reduces to $\delta = \sqrt[4]{C_1} r^{0.75}$. It has a similar form to 341 Yabuki's expression $\delta = 5.10 \times 10^{-4} r^{0.69}$, which was obtained by fitting their experimental data 342 [38]. Fig. 4b displays the microlayer profiles predicted by our hybrid model and the comparison 343 344 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 to the bubble growth time [34,35], expressed as $\delta = C_{\sqrt{\nu t_q}}$. The bubble growth time t_q can be 346 347 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.

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

models and experiment data. Microlayer profile predictions in the blue region and red region arebased 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 $P_{\nu} - P_l = \kappa_1 + P_d$ 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 the interpretation of Eq. 1. The calculated results are used to determine C_1 and C_2 in Eq. 5. We 382 383 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 µm 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 μ m has been 390 assumed compared to the 3 µm in Guion's work. It directly shows the significance of the bubble 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 391 392 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.

Finally, we discuss the microlayer profile on a weakly hydrophilic surface. As shown in **Fig. 5b**, on a surface with the Young contact angle of 75.08° the microlayer thickness predicted by the hybrid model increases to ~10 μ m at 0.5 mm length. Nevertheless, the required cavity radius (*i.e.*, nucleus size) to activate the nucleation is influenced by surface wettability. Previous studies based on thermodynamic analyses suggested a negative correlation between the critical cavity radius and 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 µm 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 $r_c = 0.5 \mu m$. 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

Fig. 5. Deviation of the microlayer profile. (a) Impact of the nonlinear-coupled effect on microlayer profile and comparison with DNS simulations. The green dashed line is from the simulation of Guion *et al.*; the blue dashed line is from the simulation of Ding *et al.* (b) Microlayer profile on the weakly hydrophilic surface with and without the nonlinear-coupled effect (Young 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 thickness in the inertia-controlled bubble growth stage is determined by the nonlinear-coupledeffect, 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 resolve the long-standing disputes over the validity of the Young contact angle at the nano-scale 440 441 [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].

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

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461 **CRediT authorship contribution statement**

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

Writing – review & editing. Hao Wang: Methodology. Uwe Hampel: Conceptualization,
Methodology, Writing - review & editing, Supervision. All authors have read and agreed to the
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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