Supporting Information:
Validation of Capillarity Theory at the Nanometer-Scale II: Stability and Rupture of Water Capillary Bridges in Contact with Hydrophobic and Hydrophilic Surfaces

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I. ANALYTICAL SOLUTION FOR AXISYMMETRIC CAPILLARY BRIDGES

We introduce the expressions for the capillary adhesion force $F_{\rm z}$ and pressure P induced by the AS bridge on the walls, and surface free energy $\mathcal{F}$. The mathematical proof of these expressions for $\theta < 90^{\rm o}$ can be found in ref [1] and hence, we only summarize the main results. For the case $\theta > 90^{\rm o}$, we provide a detailed proof of the expressions for $\mathcal{F}$, $F_{\rm z}$ and P that follow from CT.

a. Solution for $\theta < 90^{\rm o}$: $F_{\rm z}$, P, and $\mathcal{F}$ can be expressed in terms of elliptic integrals [1]. These expressions depend solely on the AS bridge volume Ω, walls separation h, water contact angle θ, and the ratio $a = A/r_{\rm b}$, where A is the minimum distance from the profile of AS bridge $r(z)$ to the z-axis and $r_{\rm b}$ is the base radius. The values of Ω, h, and θ are supposed to be known. The quantity a can be determined numerically from the equation

$$\Omega = \frac{\pi h^3}{4}\omega(a) \ , \tag{1}$$

where

$$\omega(a) = \frac{v(a,1)}{u(a,1)^3} \ ,$$

and the auxiliary functions $u(a,1)$ and $v(a,1)$ can be expressed in terms of Legendre elliptic integrals $F(k,\phi)$ and $E(k,\phi)$,

$$\begin{aligned} u(a,\zeta) =&\ a\tilde{F}(k,\phi_\zeta) + b\tilde{E}(k,\phi_\zeta), \\ v(a,\zeta) =&\ \Big[-\mathcal{R}(a,\zeta) - a^2 b\tilde{F}(k,\phi_\zeta) \\ &+b[3ab + 2(a^2+b^2)]\tilde{E}(k,\phi_\zeta)\Big]/3 \ . \end{aligned} \tag{2}$$

In these expressions,

$$\begin{aligned} b =&\ \left(\tfrac{1-a\sin\theta}{\sin\theta - a}\right) \ , \\ k =&\ s\sqrt{b^2-a^2}/b \, , \\ \mathcal{R}(a,\zeta) =&\ \zeta\sqrt{(\zeta^2-a^2)(b^2-\zeta^2)} \, , \\ \phi_\zeta =&\ \arcsin\sqrt{(b^2-\zeta^2)/(b^2-a^2)} \, , \\ \tilde{F}(k,\phi) =&\ F(k,\pi/2) - F(k,\phi) \, , \\ \tilde{E}(k,\phi) =&\ E(k,\pi/2) - E(k,\phi) \, . \end{aligned} \tag{3}$$

The force exerted by the AS bridge on the walls is given by

$$F_{\mathrm{z}} = \pi\gamma a \frac{h(1 - a\sin\theta)}{(1-a^2)u(a,1)} \ , \tag{4}$$

which is a monotonically decreasing function of h.

The Laplace pressure P is obtained from Young-Laplace equation ($\Delta P = 2\gamma H$) as,

$$P = 4\gamma \frac{u(a,1)\,(\sin\theta - a)}{h(1-a^2)}. \tag{5}$$

The surface free energy $\mathcal{F}$ can be written as,

$$\mathcal{F}(a) \equiv \gamma\pi h^2 \frac{2\sigma(a,1) - \cos\theta}{2u(a,1)^2} \ , \tag{6}$$

where

$$\sigma(a,r) = (b+a)b\tilde{E}(k,\phi_\zeta) \ . \tag{7}$$

The liquid-gas interface area A_{LG} can be written as,

$$A_{\mathrm{LG}} = \frac{\pi h^2}{2} \frac{\sigma(a,1)}{u(a,1)^2} \ . \tag{8}$$

It can be shown that the base radius of the AS bridge is given by

$$r_{\mathrm{b}}(a) = \left(\frac{4\Omega}{\pi v(a,1)}\right)^{1/3} \ , \tag{9}$$

and the liquid-solid area of one interface is given by

$$A_{\mathrm{LS}} = \pi r_{\mathrm{b}}(a)^2 = \pi \left(\frac{4\Omega}{\pi v(a,1)}\right)^{2/3} \ . \tag{10}$$

The surface tension component of capillary adhesion force F_γ is given by,

$$F_\gamma(a) = 2\pi\gamma r_{\mathrm{b}} \sin\theta = 2\pi\gamma\sin\theta \left(\frac{4\Omega}{\pi v(a,1)}\right)^{1/3} \ , \tag{11}$$

and the Laplace pressure component of capillary adhesion force F_{P} is given by,

$$F_{\mathrm{P}}(a) = \pi r_{\mathrm{b}}^2(a) P = 4\pi\gamma \frac{u(a,1)\,(\sin\theta - a)}{h\,(1-a^2)} \left(\frac{4\Omega}{\pi v(a,1)}\right)^{2/3} \ . \tag{12}$$

b. Solution for $\theta > 90^{\mathrm{o}}$: We follow the same procedure of ref [1] and consider the profile of AS bridge $z(r)$ given by

$$dr \frac{Hr^2 + C}{\sqrt{r^2 - (Hr^2 + C)^2}} = \pm dz \ ,$$

where C is a constant given by

$$\begin{aligned} AB &= C/H \ , \\ A^2 + B^2 &= 1/H^2 - 2C/H \ . \end{aligned} \tag{13}$$

In these expressions, A and B are, respectively, the minimum and maximum distance from the profile of AS bridge $r(z)$ to the z-axis. It can also be shown that $C = F_{\mathrm{z}}/2\pi\gamma$. Thus, the formal solution for $z(r)$ is

$$z(r) = \pm \int_r^B \frac{dx(AB + x^2)}{\sqrt{(B^2 - x^2)(x^2 - A^2)}} + z_0 \ . \tag{14}$$

We can rewrite the eq 14 using normalized variables for A and B: $a \equiv A/r_{\mathrm{b}}$, $b \equiv B/r_{\mathrm{b}}$, $\zeta \equiv r/r_{\mathrm{b}} \in [1, b]$:

$$u(b, \zeta) \equiv \frac{z(r)}{r_{\mathrm{b}}} \equiv \int_\zeta^b \frac{(ab + x^2)dx}{\sqrt{(x^2 - a^2)(b^2 - x^2)}} \ . \tag{15}$$

The normalized profile of AS bridge $z(r)$ is given by

$$z(r) \equiv \pm \frac{hu\,(b, 2r\Lambda/h)}{\Lambda} \ ,$$

where it is define the quantity

$$\Lambda(b) \equiv u(b, 1) = h/(2r_{\mathrm{b}}) \ . \tag{16}$$

It follows that $z[h/(2\Lambda)] = \pm h/2$. We note that the parameters a and b in eq 15 are not independent. Specifically, by applying the boundary condition for the contact angle θ formed between the AS bridge and the plates

$$\left.\frac{dz}{dr}\right|_{\pm h/(2\Lambda)} = \pm \tan\theta \ , \tag{17}$$

one can show that

$$a(b) = \left(\frac{1 - b\sin\theta}{\sin\theta - b} \right) \ , \tag{18}$$

where $0 \leq a \leq 1$.

In general, the integral eq 15 is an elliptical function. In a special case $b \to 1/\sin\theta$, $a \to 0$, the integral can be expressed in arcsines, and the surface becomes a sphere [2].

The quantity b can be determined numerically by integrating eq 15 by parts. Specifically, $\pi u^2(b,\zeta) - 2\pi \int_0^\zeta u(b,x)xdx = \pi \int_0^\zeta x^2 du$ from which it follows that the volume Ω formed by the surface $z(r)$ and the plates at $z = \pm h/2$ is given by

$$\Omega = \frac{\pi h^3}{4} \omega(b) \ , \tag{19}$$

where

$$\omega(b) \equiv \frac{v(b,1)}{\Lambda^3} \ , \tag{20}$$

and

$$v(b,\zeta) \equiv s \int_\zeta^b \frac{x^2(ab + x^2)dx}{\sqrt{(x^2 - a^2)(b^2 - x^2)}} \ . \tag{21}$$

Since h, Ω, and θ are known, the parameter b, which can be obtained numerically from eq 19, defines the profile of AS bridge $z(r)$. As we show next, these variables also define F_z, F_γ, P, F_P, and $\mathcal{F}$.

Using eqs 13, 16, and 18 we can obtain the average curvature H

$$H = \frac{2\Lambda(\sin\theta - b)}{h(1 - b^2)} > 0 \ , \tag{22}$$

and the capillary adhesion force $F_\mathrm{z} = 2\pi\gamma C$ can be expressed as follows,

$$F_\mathrm{z} = \pi\gamma b \frac{h(1 - b\sin\theta)}{\Lambda(1 - b^2)} \ . \tag{23}$$

Note that F_z can change the sign from attractive (positive) for $b > 1/\sin\theta$ to repulsive (negative) for $b < 1/\sin\theta$.

The base radius of AS bridge can be found from:

$$r_\mathrm{b} = h/(2\Lambda(b)) = \left(\frac{4\Omega}{\pi v(b,1)} \right)^{1/3} \ . \tag{24}$$

Hence, the surface tension force F_γ can be calculated from:

$$F_\gamma(b) = 2\pi\gamma r_\mathrm{b}\sin\theta = 2\pi\gamma\sin\theta\left(\frac{4\Omega}{\pi v(b,1)}\right)^{1/3} . \tag{25}$$

The Laplace pressure component F_P of F_z can be obtained from the Laplace pressure P inside the AS bridge, which can be found from Young-Laplace equation and eq 22:

$$P = 2\gamma H = 4\gamma\frac{u(b,1)\,(\sin\theta - b)}{h\,(1-b^2)} . \tag{26}$$

Then, the F_P is obtained as

$$F_\mathrm{P}(b) = \pi r_\mathrm{b}^2 P = 4\pi\gamma\frac{u(b,1)\,(\sin\theta - b)}{h\,(1-b^2)}\left(\frac{4\Omega}{\pi v(b,1)}\right)^{2/3} . \tag{27}$$

To calculate the surface free energy $\mathcal{F}$, we need to find the liquid-gas interface area A_LG. It can be shown that

$$A_\mathrm{LG} = 2\pi\sigma(b,1)h^2/\Lambda^2 \tag{28}$$

where

$$\sigma(b,\zeta) \equiv s\int_\zeta^b \frac{(b+a)x^2dx}{\sqrt{(x^2-a^2)(b^2-x^2)}} \tag{29}$$

can be found using elementary formulas for the rotational surface area. One can express $u(b,\zeta)$, $\sigma(b,\zeta)$ and $v(b,\zeta)$ in terms of the Legendre elliptic integrals of the first and the second kind by the same variable substitution as in case $\theta < 90^\mathrm{o}$, $\phi_\zeta = \arcsin\sqrt{(b^2-\zeta^2)/(b^2-a^2)}$. Now, we have

$$\sigma(b,\zeta) = (b+a)bE(k,\phi_\zeta) \tag{30}$$

and,

$$u(b,\zeta) = bF(k,\phi_\zeta) + bE(k,\phi_\zeta), \tag{31}$$

where $k = \sqrt{b^2-a^2}/b$. Finally, partial integration yields

$$v(b,\zeta) = \left[\mathcal{R}(b,\zeta) - a^2bF(k,\phi_\zeta) + b[3ab + 2(a^2+b^2)]E(k,\phi_\zeta)\right]/3 , \tag{32}$$

where $\mathcal{R}(b,\zeta) = \zeta\sqrt{(\zeta^2-a^2)(b^2-\zeta^2)}$, in particular, $\mathcal{R}(b,1) = -\cos\theta(1-b^2)/(\sin\theta - b)$, and $\mathcal{R}(b,ab) = -a^2b^2\cos\theta(1-b^2)/(\sin\theta-b)$.

Therefore, the surface free energy $\mathcal{F} = \gamma(A_{\mathrm{LG}} - \cos\theta A_{\mathrm{LS}})$ is obtained by using eq 28 and the equation

$$A_{\mathrm{LS}} = 2\pi r_{\mathrm{b}}^2(b)\ , \tag{33}$$

where $r_{\mathrm{b}}^2(b)$ is given by eq. 24. Thus

$$\mathcal{F}(b) \equiv \gamma\pi h^2 \frac{2\sigma(b,1)-\cos\theta}{2\Lambda^2}\ . \tag{34}$$

Analogously to the case $\theta < 90^{\mathrm{o}}$ [1], solving eq 19 with respect to b gives us all the properties of the AS bridge. Now, $\omega(b)$ is a non-monotonic function of b with a single minimum at $b = b_0(\theta)$, which can be found as a single root of the equation

$$\frac{d\omega}{db} = \frac{(A_0F^2 + 2B_0FE + C_0E^2 + 2D_0F + 2E_0E + F_0)(b^2-1)}{\Lambda^4(b^2-2b\sin\theta+1)(b-\sin\theta)} = 0, \tag{35}$$

where A_0, B_0, C_0, D_0, E_0, and F_0 are rational functions of b, $\sin\theta$, and $\cos\theta$, given by:

$$\begin{aligned}
A_0 &= -\tfrac{\sin\theta(1-b\sin\theta)^2[b-\cot(\theta/2)][b-\tan(\theta/2)]}{(b-\sin\theta)^3}\\
B_0 &= \tfrac{\sin\theta[1-2b\sin\theta+2b^2\sin^2\theta-2b^3\sin\theta+b^4][b-\cot(\theta/2)][b-\tan(\theta/2)]}{(b-\sin\theta)^3}\\
C_0 &= -3\tfrac{b^2\sin\theta[b-\cot(\theta/2)][b-\tan(\theta/2)]}{b-\sin\theta}\\
D_0 &= \tfrac{\cos\theta(\sin\theta-2b(1+\sin^2\theta)+2b^2(\sin\theta+\sin^3\theta)+2b^3\cos^2\theta-b^4\sin\theta)}{2b(b-\sin\theta)^2}\\
E_0 &= -\tfrac{\cos\theta b(2-\sin^2\theta+b\sin\theta-2b^2)}{(b-\sin\theta)}\\
F_0 &= -2\cos^2\theta\ .
\end{aligned} \tag{36}$$

We conclude by calculating the critical height $h_{\max}$. Analogous considerations as for $\theta < 90^{\mathrm{o}}$ [1] gives the condition of stability $b < b_{\mathrm{c}} = \tan(\theta/2)$. However, for $\theta > 90^{\mathrm{o}}$, one has $b_0 > b_{\mathrm{c}}$. Accordingly, for $\theta > 90^{\mathrm{o}}$, the AS bridge always breaks asymmetrically for $\Omega/2\pi h^3 \leq \omega(b_{\mathrm{c}})$. The equations for $\Lambda(b_{\mathrm{c}})$, $\sigma(b_{\mathrm{c}})$, and $v(b_{\mathrm{c}})$ coincide with the equations $\Lambda(a_{\mathrm{c}})$, $\sigma(a_{\mathrm{c}})$, and $v(a_{\mathrm{c}})$, see ref [1]. Thus, the maximum stable height for AS bridge $h_{\mathrm{max,a}}$ for $\theta > 90^{\mathrm{o}}$ is given by

$$h_{\mathrm{max,a}} = \left(\frac{4\Omega}{\pi\omega(b_{\mathrm{c}},1)}\right)^{\frac{1}{3}}\ . \tag{37}$$

II. COMPLETE SET OF FIGURES

The main manuscript includes the average profiles of AS bridges in equilibrium for selected surface polarities k (Figure 2). In Figure S1, we include the average profiles of equilibrium AS bridges for all surface polarities studied. Similarly, the main manuscript (Figure 7) shows the time evolution of the AS bridges during the rupture process at the critical wall–wall separation $h = h_{\mathrm{C'}}$ for selected values of k. The time evolution of the AS bridges at $h = h_{\mathrm{C'}}$ and for all cases studied are included in Figure S2. The time evolution of the AS bridges at $h = h_{\mathrm{C}}$ is shown in Figure S4. Snapshots of the AS bridges at the rupture time τ_{r}, for the AS bridges included in Figures S2 and S4, are shown in Figures S3 and S5.

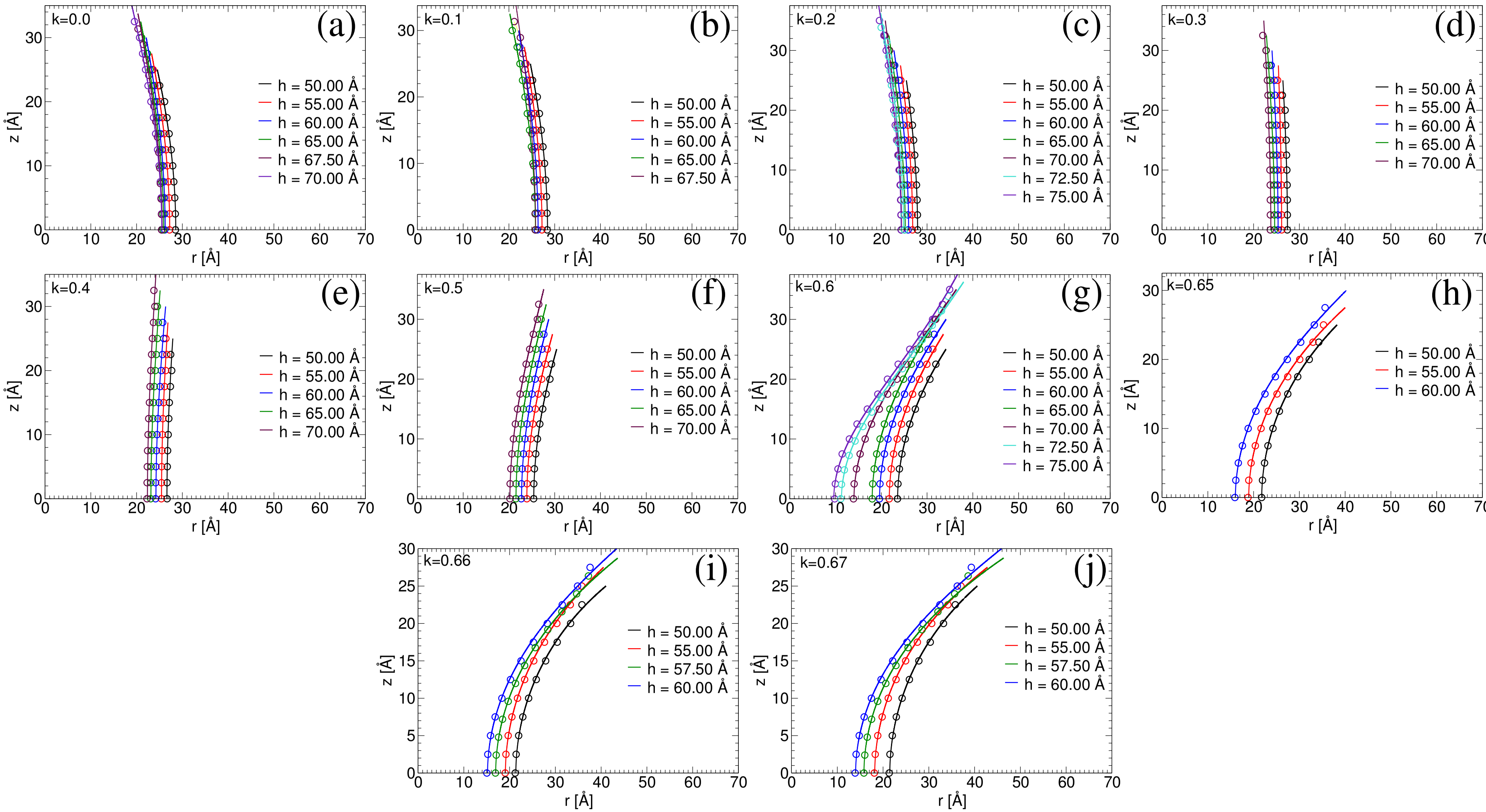

Figure S1: Average profiles of stable AS bridges, height as a function of *radius* r, calculated from MD simulations (circles), for different wall–wall separations h. Only the upper half ($z > 0$) of the AS bridge is shown for clarity. The lines are the best fits obtained from CT using eq 2. The Figures a–j correspond, respectively, to surfaces with polarity $k = 0.0$ to 0.67.

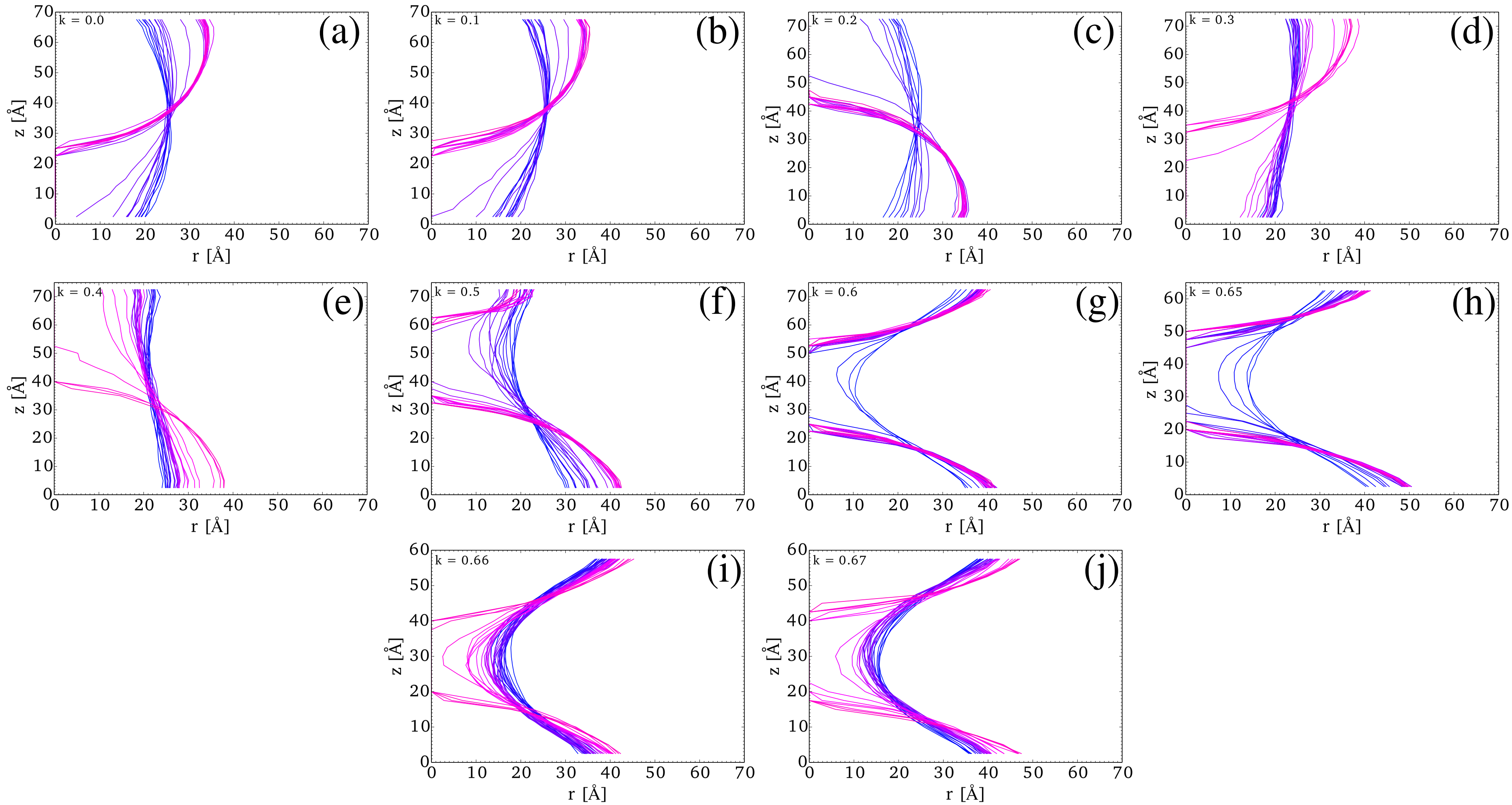

Figure S2: Profiles of AS bridges during rupture at the critical walls separation $h_{C'}$. Each profile is obtained over a time window of 0.1 ns, and the gradient color shows the time evolution of AS bridge; time increases from blue to magenta profiles. The Figures a–j correspond, respectively, to surfaces with polarity $k = 0.0$ to 0.67.

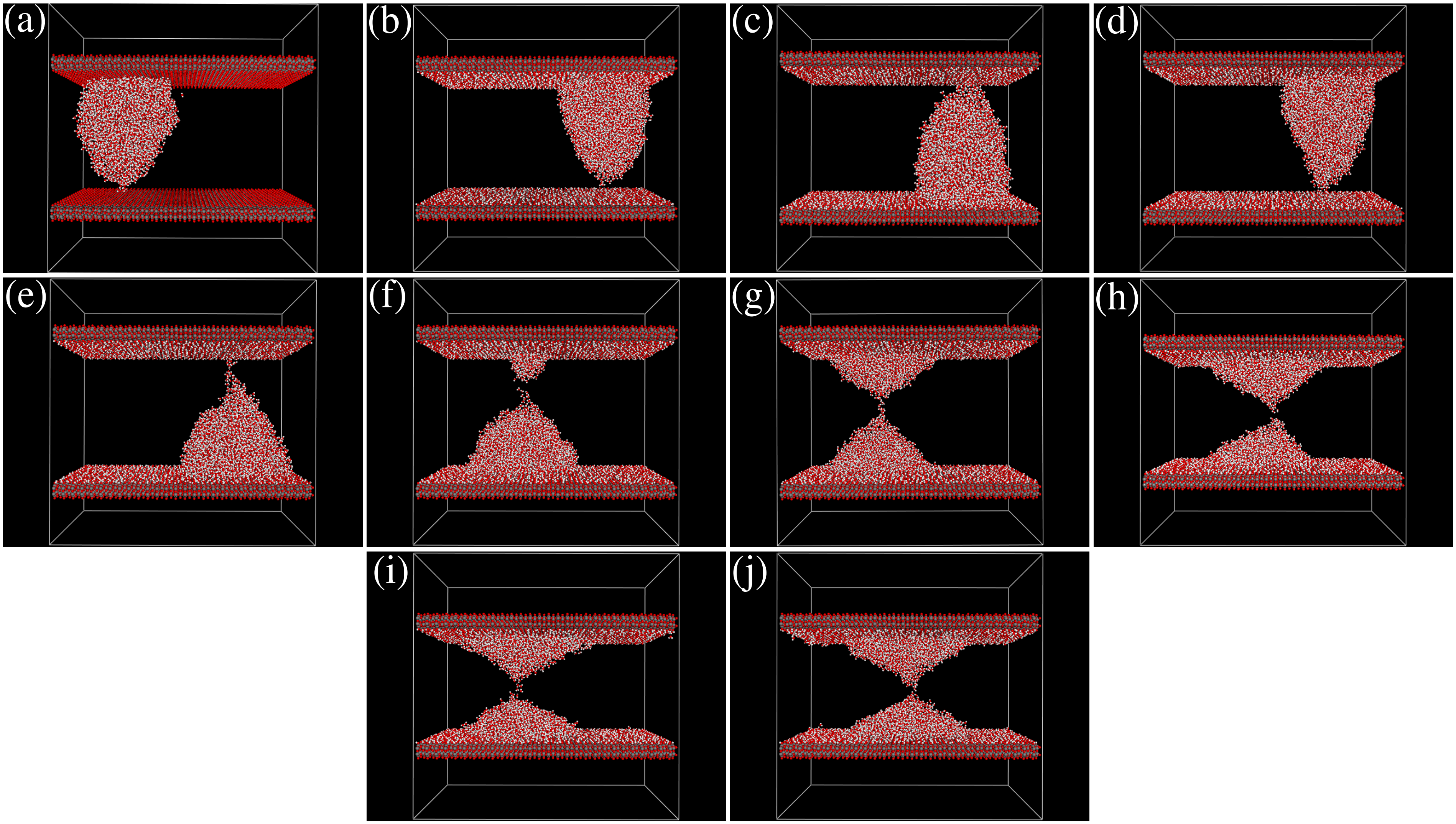

Figure S3: Snapshots of AS bridges at the critical rupture time τ_r and at the critical walls separation $h_{C'}$. In (a), there are no hydrogen atom attached to the surface ($k = 0.0$). The Figures a–j correspond, respectively, to surfaces with polarity $k = 0.0$ to 0.67.

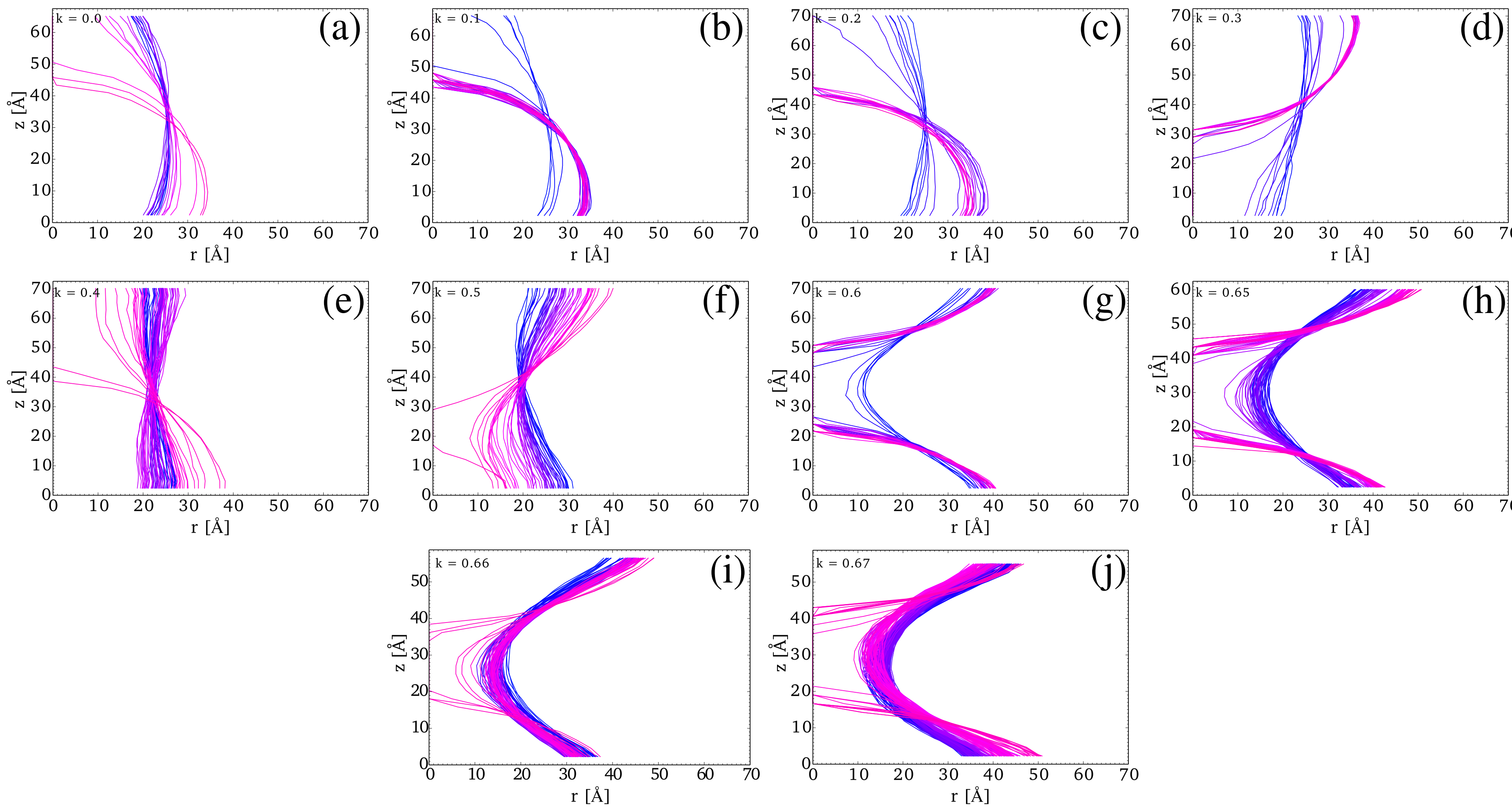

Figure S4: Profiles of AS bridges during its rupture at the critical walls separation h_{C}. Each profile is obtained over a time window of 0.1 ns, and the gradient color shows the time evolution of AS bridge; time increases from blue to magenta profiles. The Figures a–j correspond, respectively, to surfaces with polarity $k = 0.0$ to 0.67.

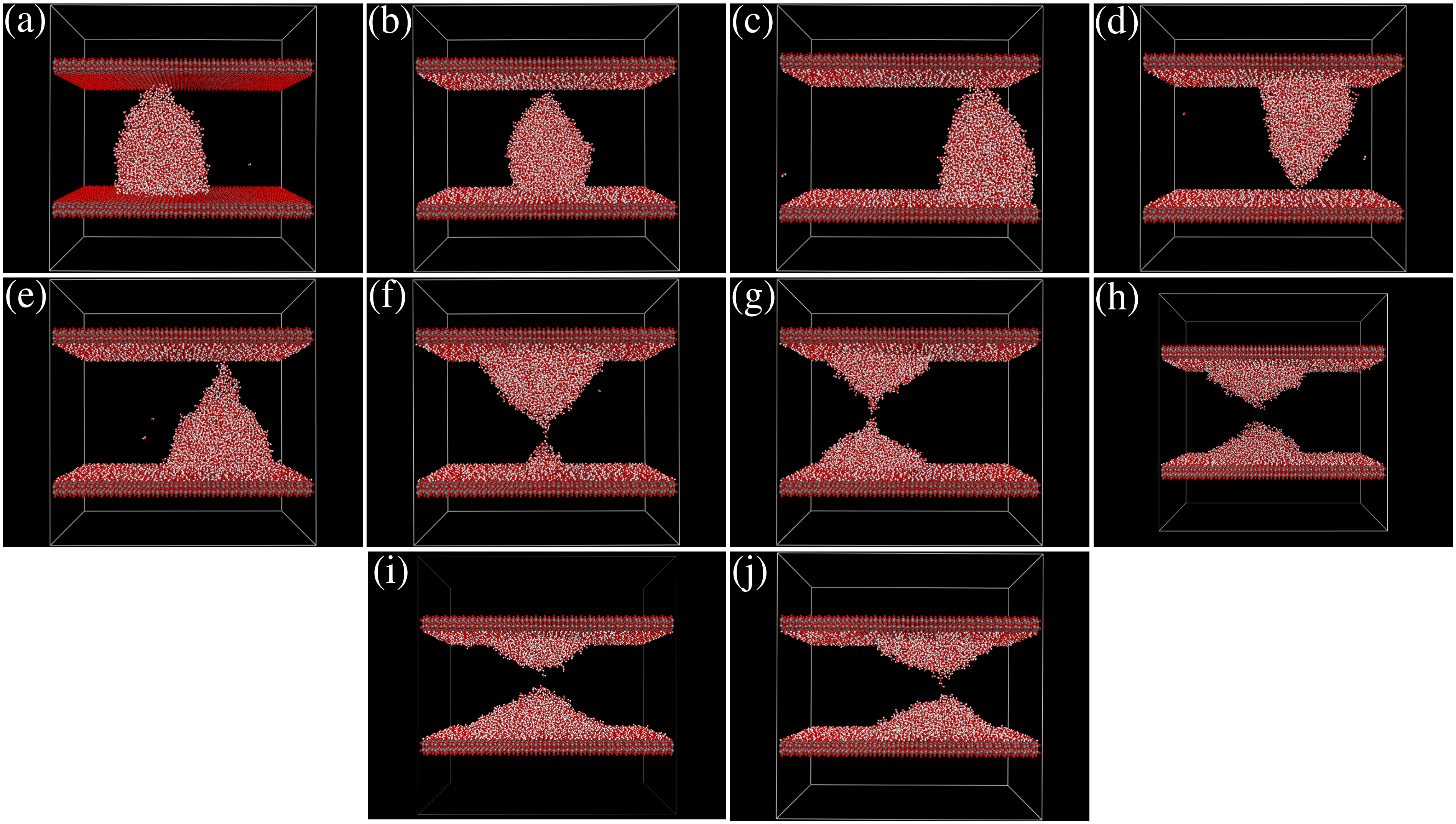

Figure S5: Snapshots of AS bridges at the critical rupture time τ_{r} and at the critical walls separation h_{C}. In (a), there are no hydrogen atom attached to the surface ($k = 0.0$). The Figures a–j correspond, respectively, to surfaces with polarity $k = 0.0$ to 0.67.

[1] Alencar, A. M.; Wolfe, E.; Buldyrev, S. V. Monte Carlo Simulation of Liquid Bridge Rupture: Application to Lung Physiology. *Phys. Rev. E* **2006**, *74*, 026311.

[2] Zhou, L. On Stability of a Catenoidal Liquid Bridge. *Pac. J. Math* **1997**, *178*, 185–198.