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Nanoparticles as Universal Adhesives

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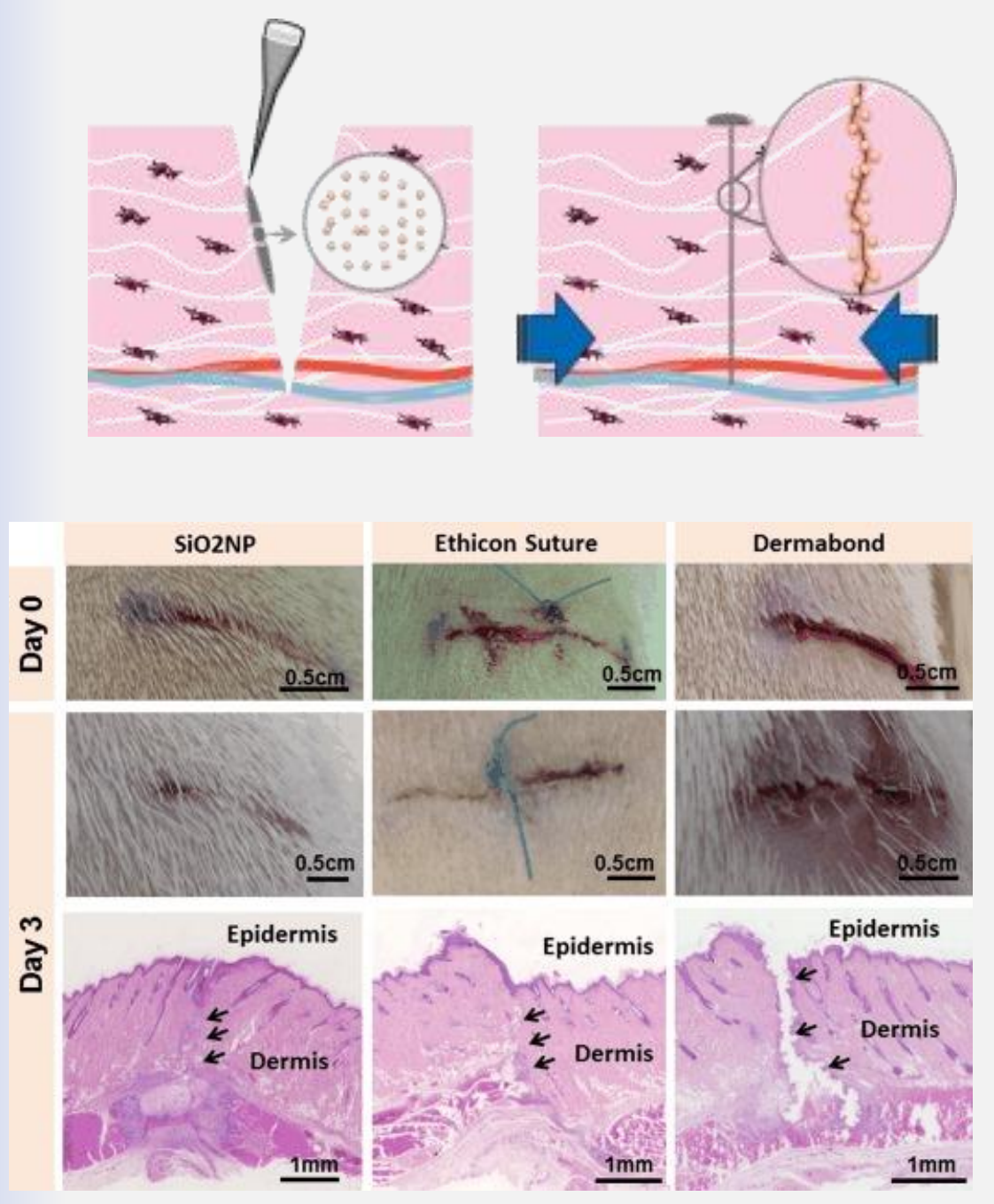
Research Group

Abstract

Nanoparticles are shown to be able to act as effective adhesives capable of binding two soft materials together. We performed coarse-grained molecular dynamics simulations to study contact mechanics of hard and soft nanoparticles at the interfaces between two elastic surfaces. Our simulations have demonstrated that a nanoparticle at the interface between two elastic substrates could be in a bridging or Pickering state. The degree of penetration of a nanoparticle into a substrate is shown to be determined by nanoparticle size, strength of nanoparticle-substrate interactions, and nanoparticle and substrate elastic properties. Using the Weighted Histogram Analysis Method, we calculated the potential of mean force for separation of two substrates which interface was reinforced by deformable nanoparticles. These simulations show that interface reinforcement is a function of nanoparticle size and elastic modulus. In particular, we have shown that the softest nanoparticles are most effective in interface reinforcement demonstrating about eight times increase in the work of adhesion.

Motivation

Glue for Biological Tissues, Gels, & Elastomers



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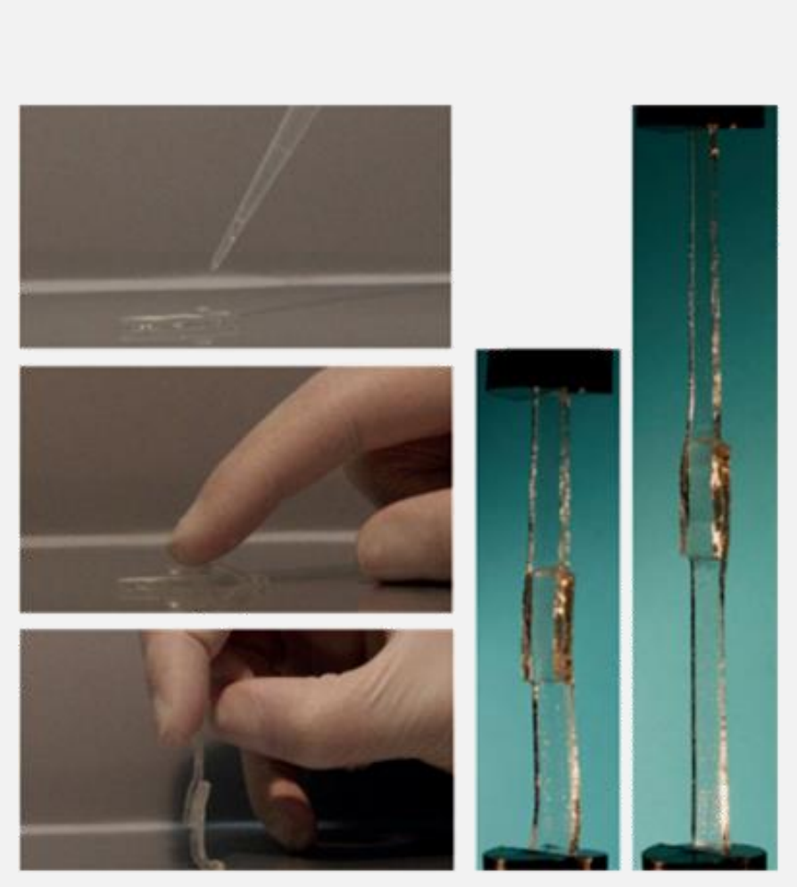
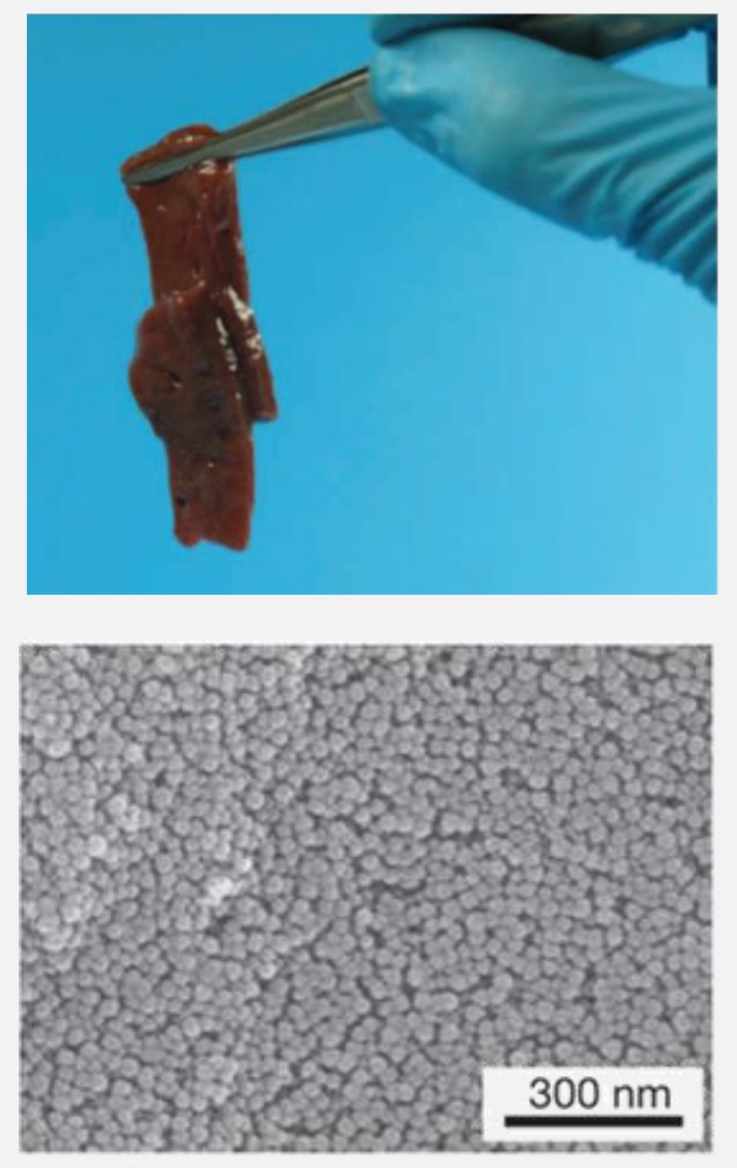


Nature **505** (2014) 382–385

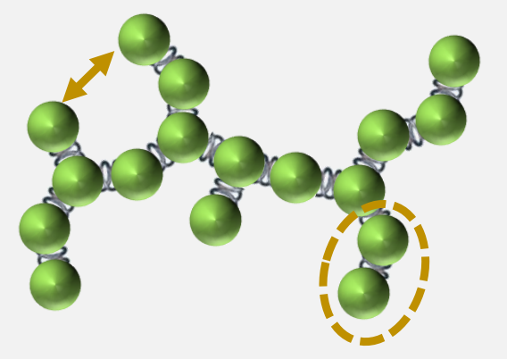


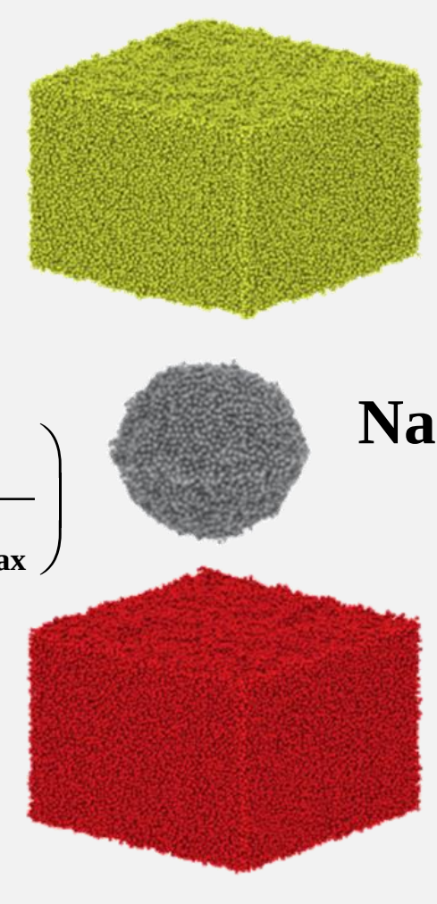
MD Simulation Details

Lennard-Jones (LJ) Potential

$$U_{LJ}(r_{ij}) = \begin{cases} 4\varepsilon_{LJ}\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6} - \left(\frac{\sigma}{r_{cut}}\right)^{12} + \left(\frac{\sigma}{r_{cut}}\right)^{6}\right] & r_{ij} \le r_{cut} \\ 0 & r_{ij} > r_{cut} \end{cases}$$

LJ Interaction Parameters	ε_{LJ} $[k_BT]$	σ	r_{cut}
Same Atom Type	*1.5*	*1.0*	*2.5*
NP - Gel	*1.2*	*1.0*	*2.5*
Gel 1 – Gel 2	*0.3*	*1.0*	*2.5*





FENE Bond Potential

$$U_{FENE}(r) = -\frac{1}{2}k_{spring}R_{\max}^2 \ln\left(1 - \frac{r^2}{R_{\max}^2}\right)$$

Langevin Thermostat
NVT Ensemble
Velocity-verlet Algorithm

Polymer chain: DP = 32, Bead diameter: σ

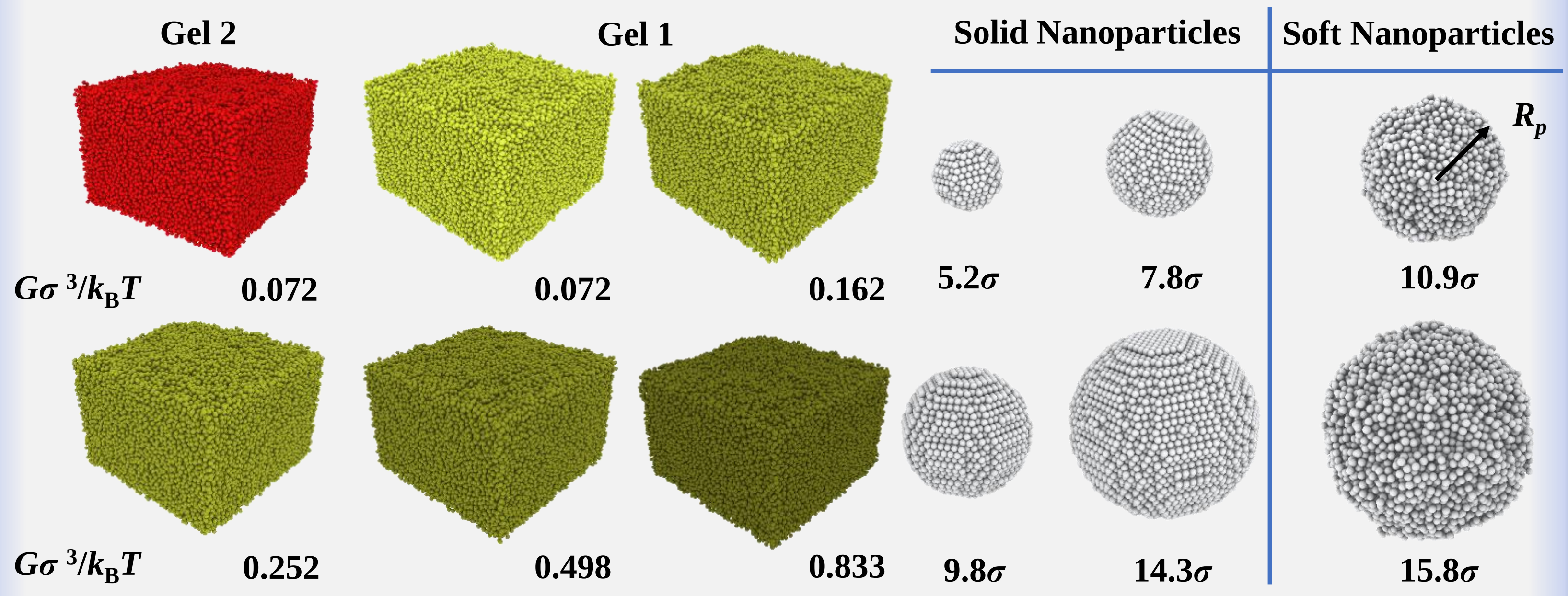
Crosslinking density ρ_c: 0.095 to 0.421 σ^{-3}

Network density: ~ $1.0\sigma^{-3}$

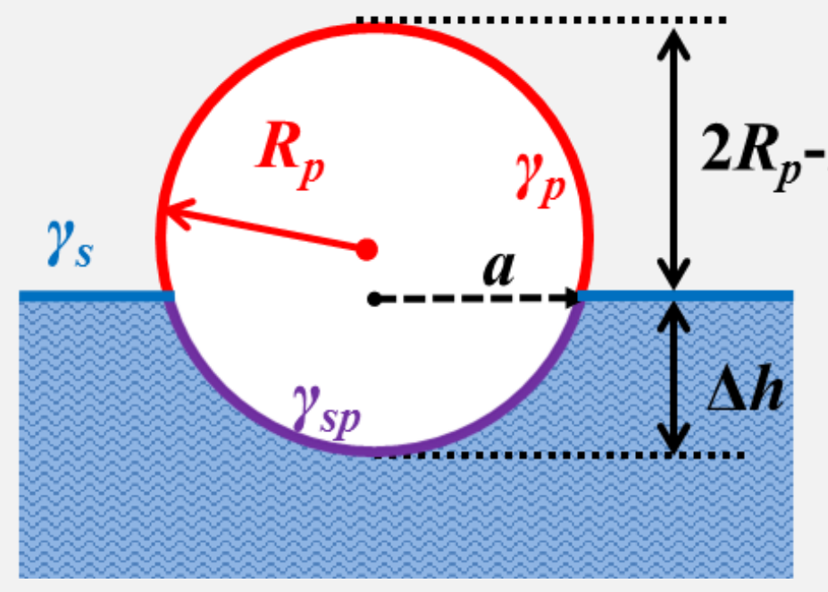
Periodic boundary in lateral directions

Equation of motion: $m\frac{d\vec{v}_i(t)}{dt} = \vec{F}_i(t) - \xi\vec{v}_i(t) + \vec{F}_i^R(t)$

δ-functional correlations:
$$\left\langle \vec{F}_i^R(t)\cdot\vec{F}_i^R(t')\right\rangle = 6k_BT\xi\delta(t-t')$$



Nanoparticle – Substrate Equilibrium Contact

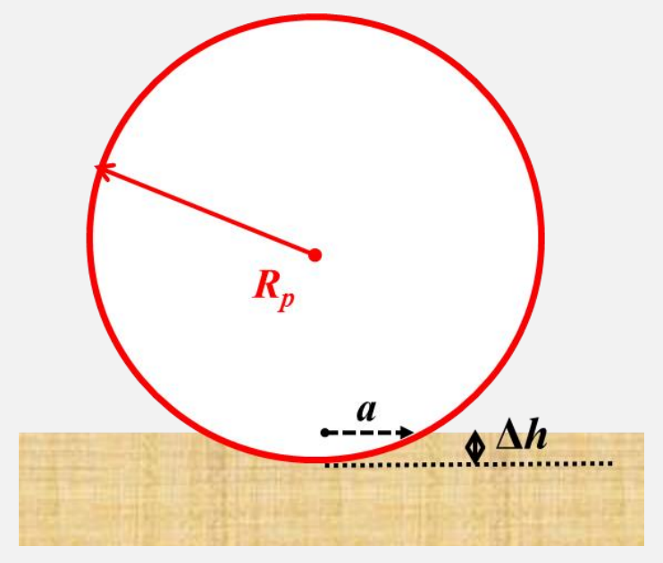


System free energy change: $\Delta F = F(\Delta h) - F(0)$

$$\Delta F = \{ (A-\pi a^2)\gamma_s + \pi(a^2+(2R_p-\Delta h)^2)\gamma_p + \pi(a^2+\Delta h^2)\gamma_p \} - \{A\gamma_s + 4\pi R_p^2\gamma_p\}$$

$\Delta F = -2\pi R_pW\Delta h + \pi\Delta h^2\gamma_s$ **Work of adhesion:** $W = \gamma_s + \gamma_p - \gamma_{sp}$

Equilibrium indentation: $\Delta h = \dfrac{R_pW}{\gamma_s}$

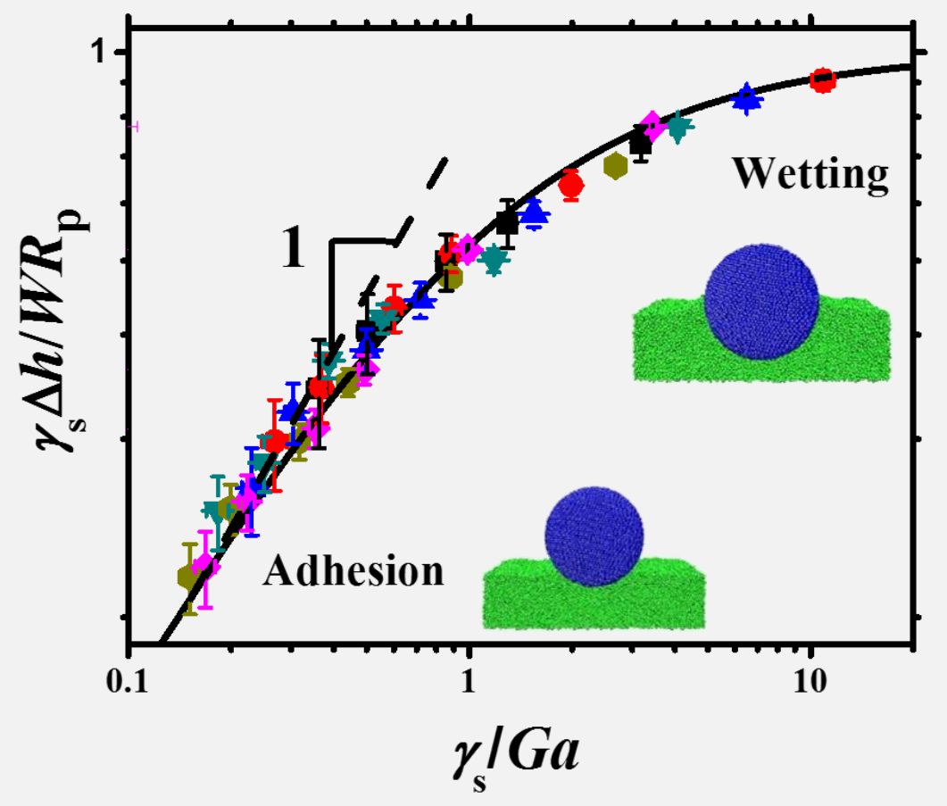


Elastic energy of contact: $\Delta U_{elast} \propto G\Delta h^2 a$

Adhesion energy of contact: $\Delta U_{adhe} = -2\pi R_p\Delta hW$

System free energy change: $\Delta F = -2\pi R_pW\Delta h + CGR_p^{1/2}\Delta h^{5/2}$

Equilibrium indentation: $\Delta h \propto \dfrac{R_p^{1/3}W^{2/3}}{G_p^{2/3}}$ **Small deformations:** $a \approx \sqrt{R_p\Delta h}$



Total Change of System Free Energy:

$$\Delta F_{Total} = -2\pi R_pW\Delta h + \pi\Delta h^2\gamma_s + CGR_p^{1/2}\Delta h^{5/2}$$

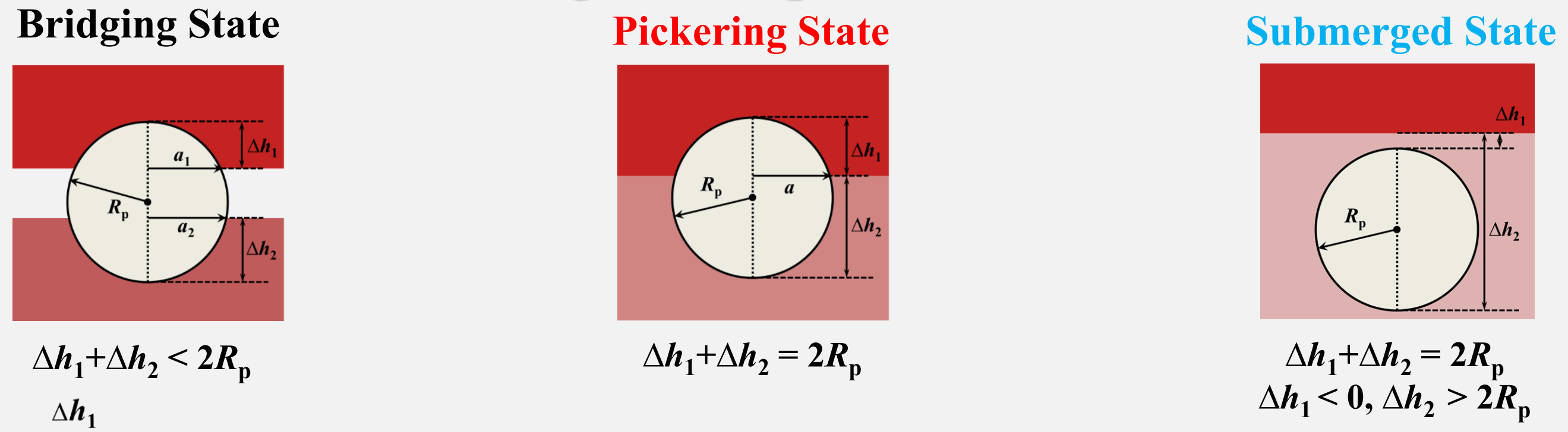
Wetting limit: $\dfrac{\gamma_s\Delta h}{WR_p} = 1$

Adhesion limit: $\dfrac{\gamma_s\Delta h}{WR_p} = \dfrac{1}{C'}\dfrac{\gamma_s}{Ga}$

$$\boxed{\frac{\gamma_s\Delta h}{WR_p} \approx \frac{1}{1+C'(\gamma_s/Ga)^{-1}}}$$

Crossover: $R_p \approx R^* = \gamma^{*3/2}G_1^{*-1}W^{-1/2}$ $\Delta h \approx \Delta h^* = \gamma^{*1/2}W^{1/2}G_1^{*-1}$

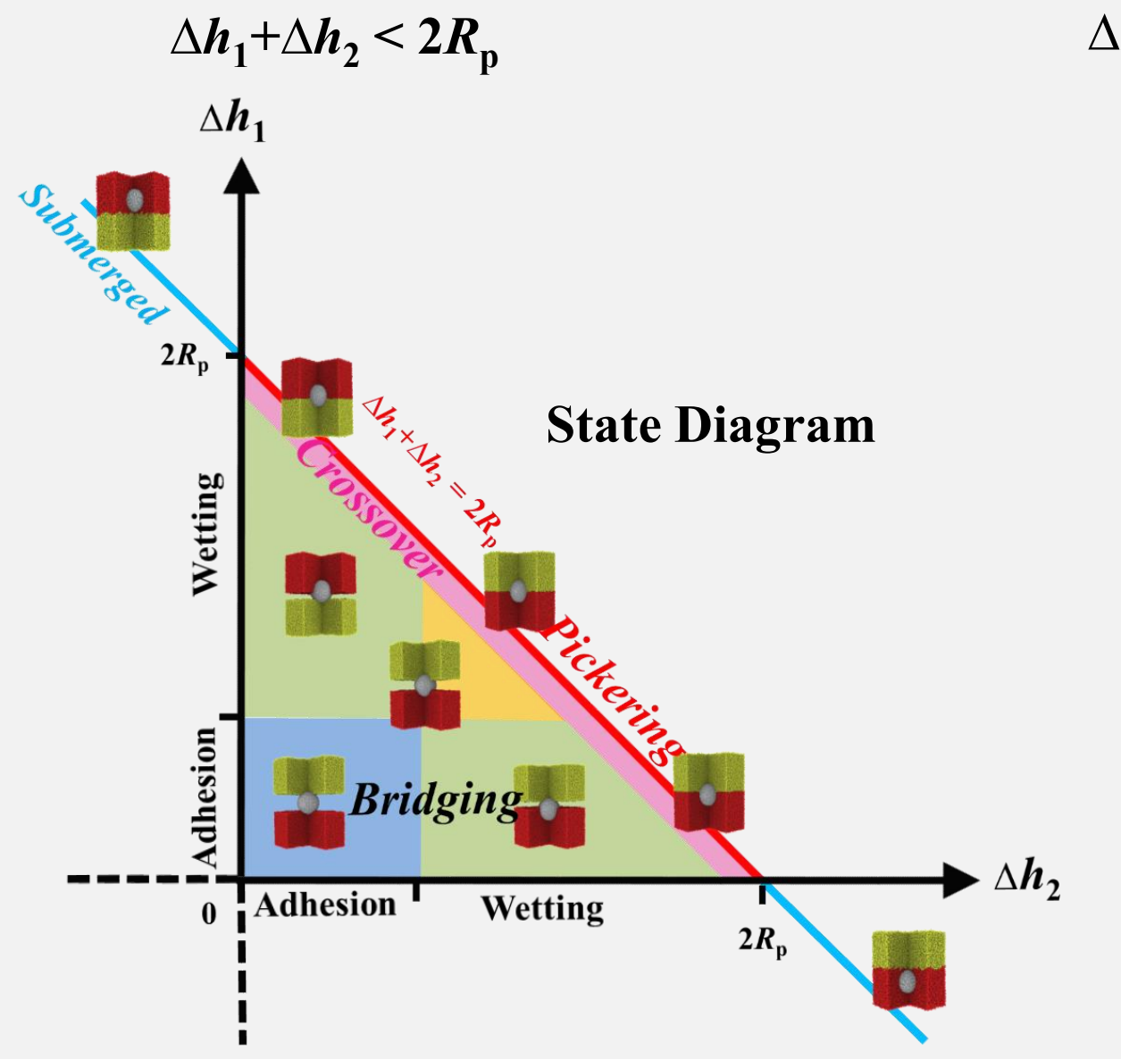
Rigid Nanoparticles

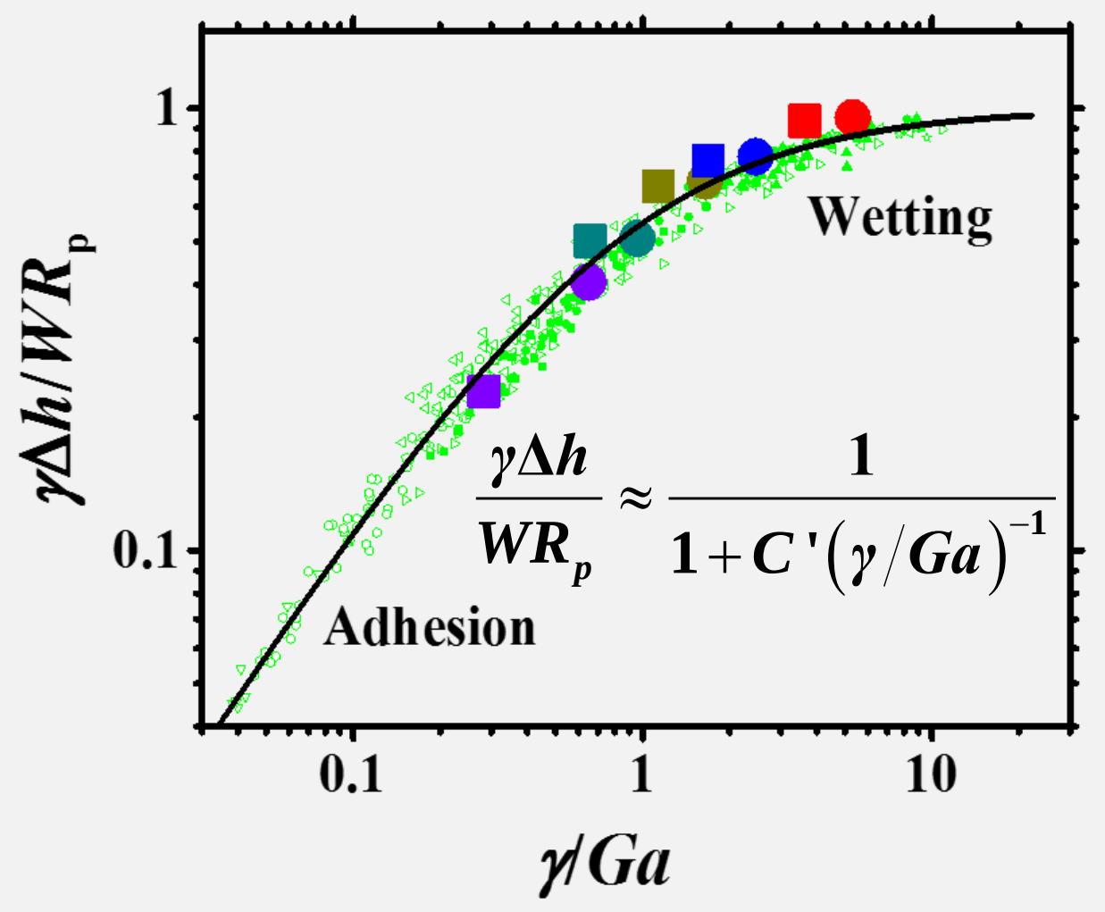


$\Delta h_1 + \Delta h_2 < 2R_p$

$\Delta h_1 + \Delta h_2 = 2R_p$

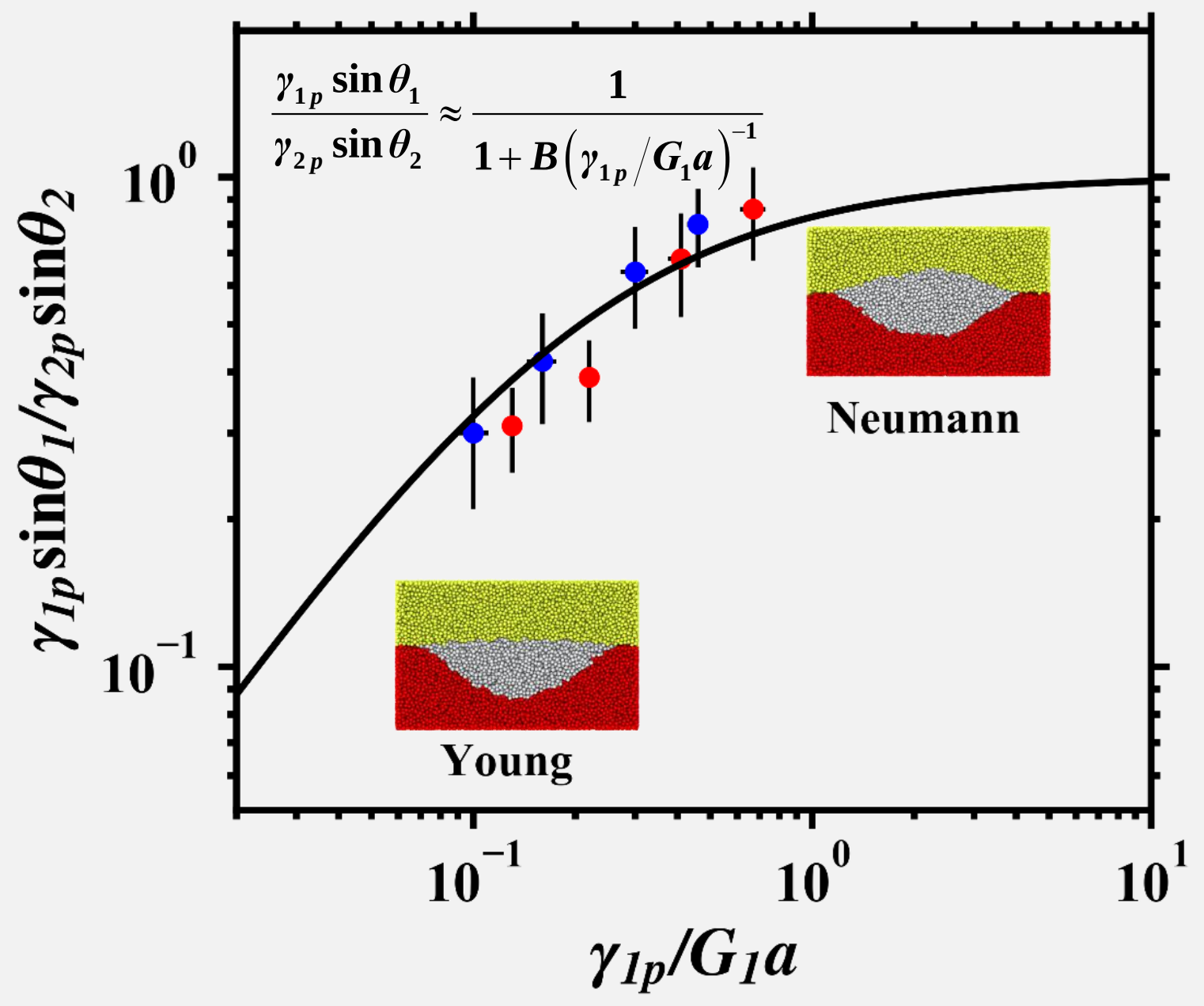
$\Delta h_1 + \Delta h_2 = 2R_p$
$\Delta h_1 < 0$, $\Delta h_2 > 2R_p$



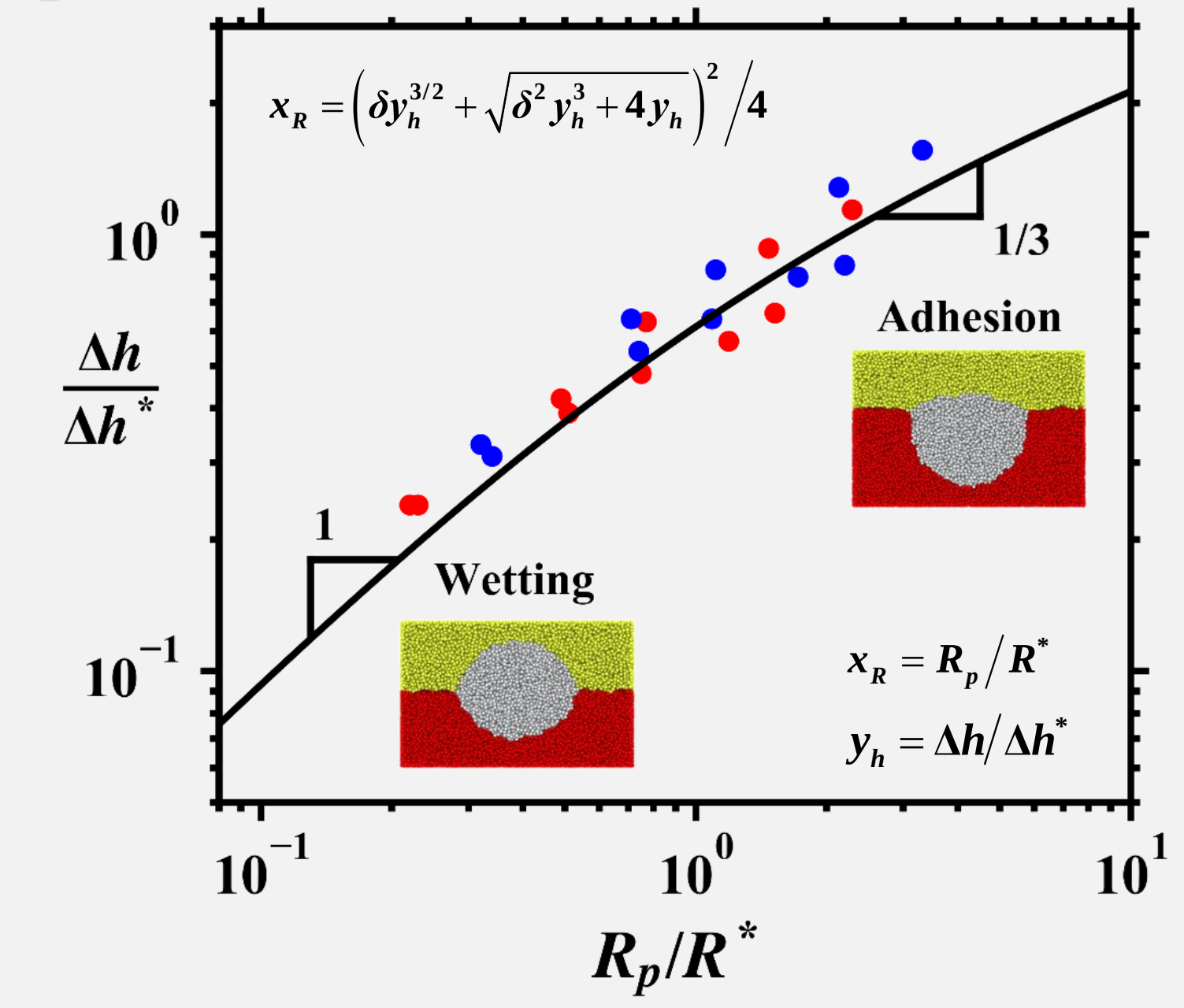


$$\frac{\gamma\Delta h}{WR_p} \approx \frac{1}{1+C'(\gamma/Ga)^{-1}}$$

Soft Nanoparticles

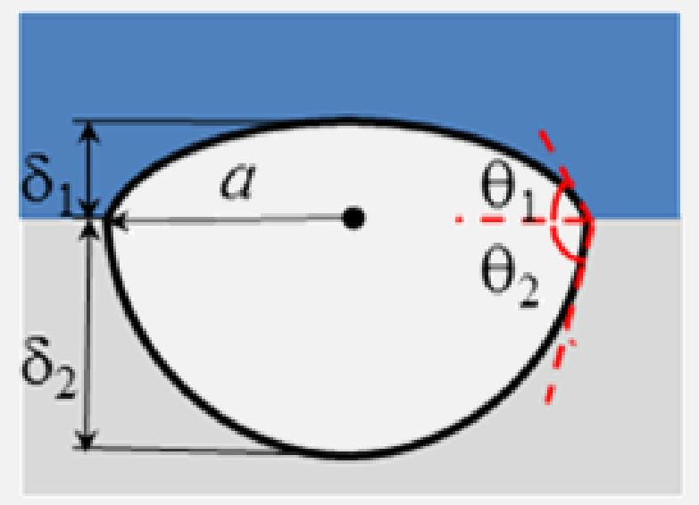


$$\frac{\gamma_{1p}\sin\theta_1}{\gamma_{2p}\sin\theta_2} \approx \frac{1}{1+B(\gamma_{1p}/G_1a)^{-1}}$$



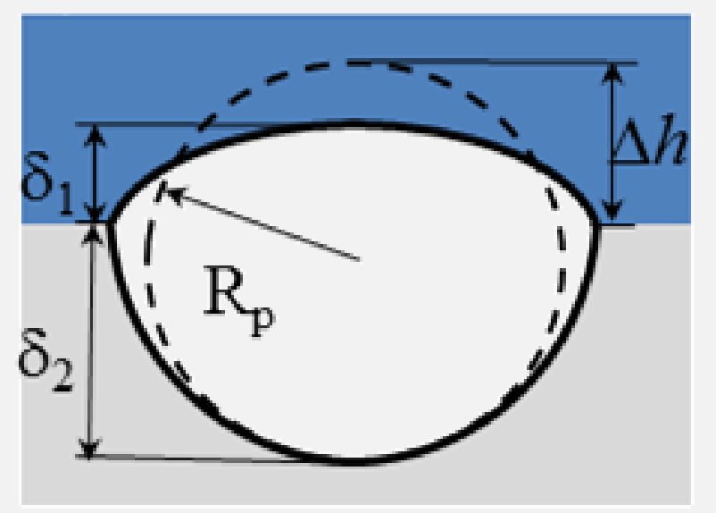
$$x_R = \left(\delta y_h^{3/2} + \sqrt{\delta^2y_h^3 + 4y_h}\right)^2/4$$

$x_R = R_p/R^*$
$y_h = \Delta h/\Delta h^*$



$$\delta_1 = \frac{1-\cos\theta_1}{\sin\theta_1}a = \tan\frac{\theta_1}{2}a$$

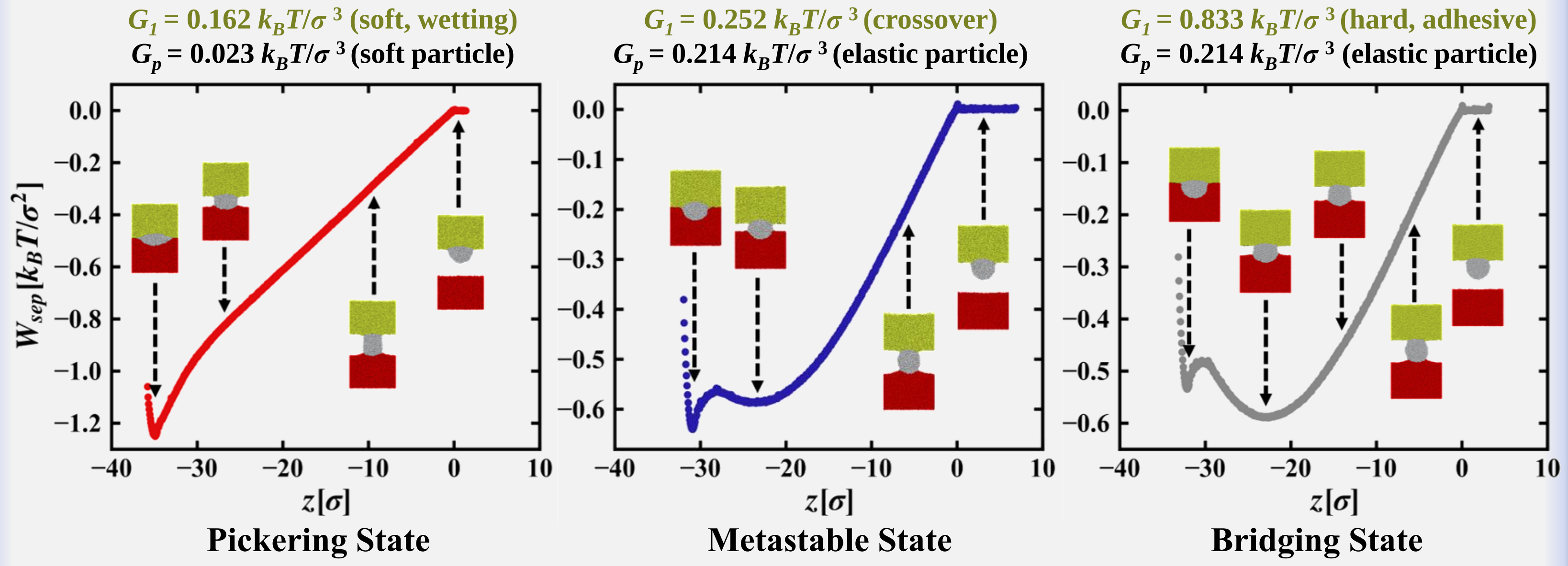
$$\delta_2 = \frac{1-\cos\theta_2}{\sin\theta_2}a = \tan\frac{\theta_2}{2}a$$



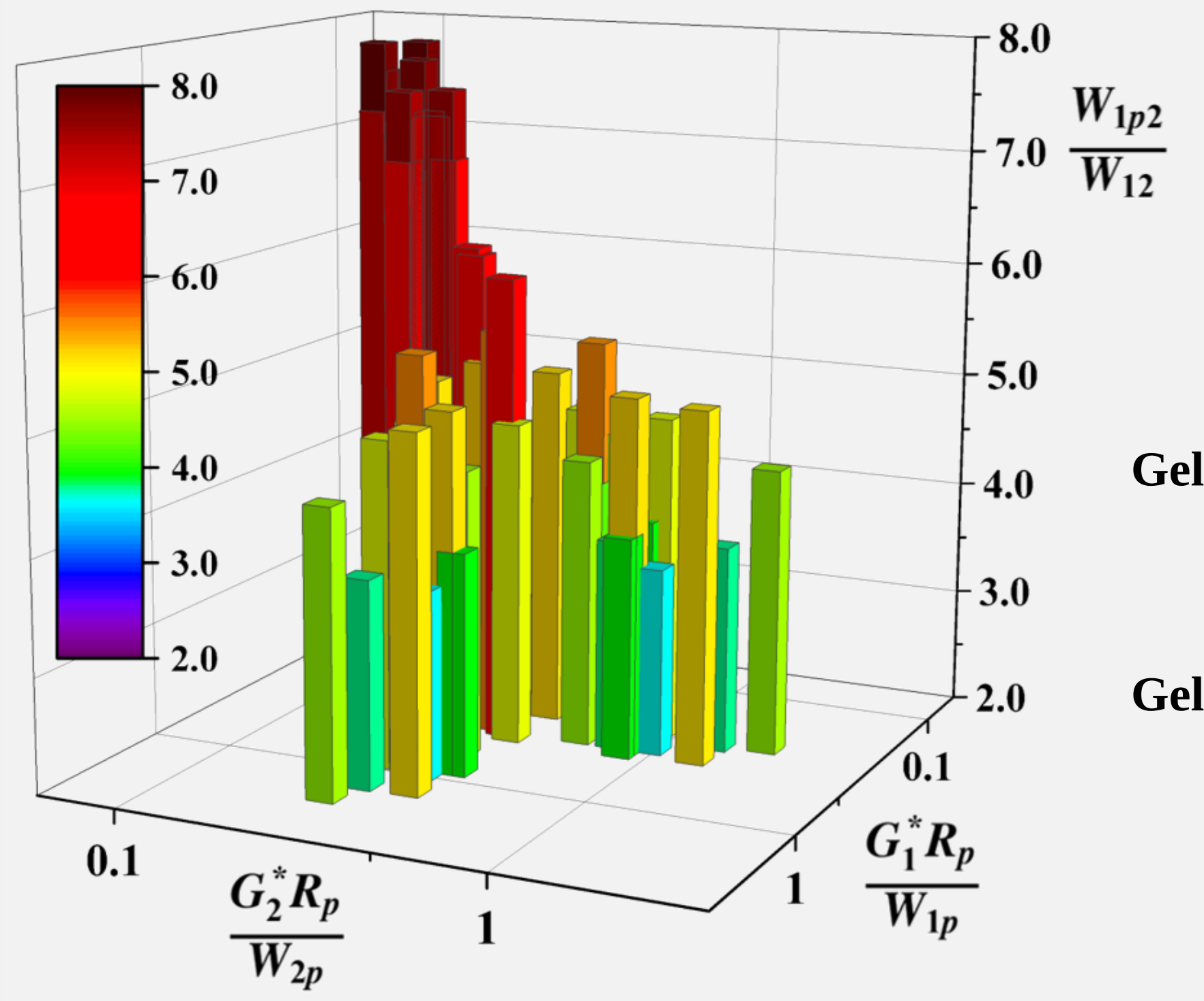
Wetting Limit:
$$\Delta h \propto \frac{R_pW}{\gamma^*}$$

Adhesion Limit:
$$\Delta h \propto \frac{R_p^{1/3}W^{2/3}}{G_1^{*2/3}}$$

Potential of Mean Force

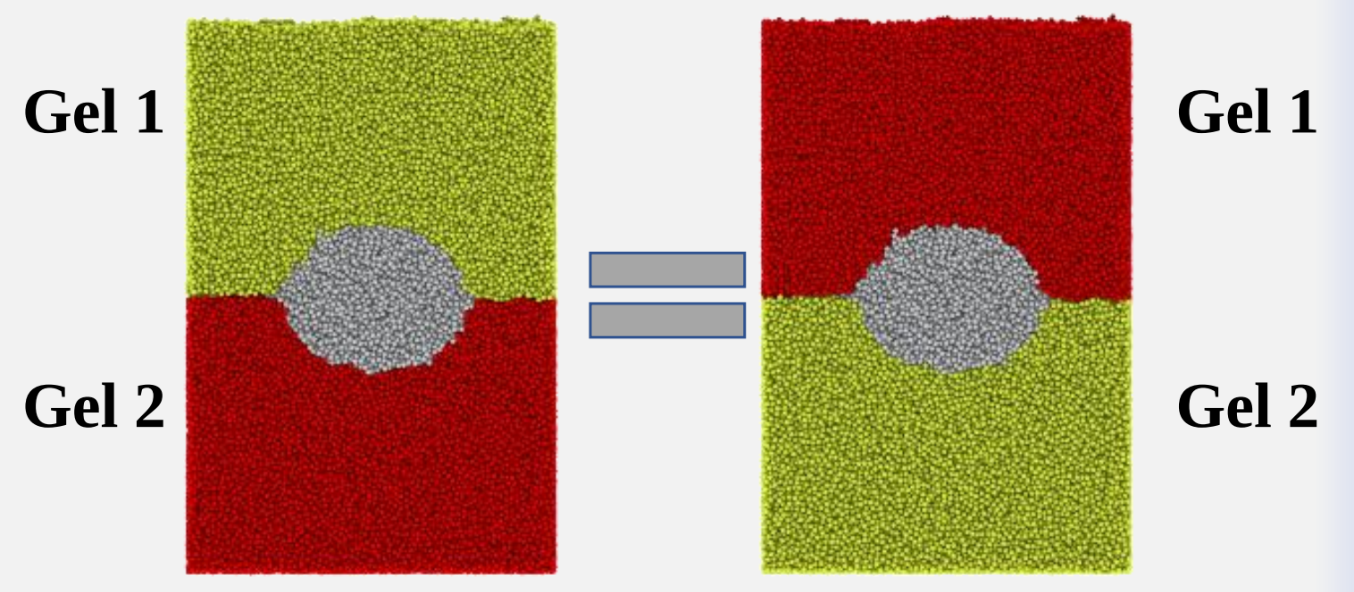


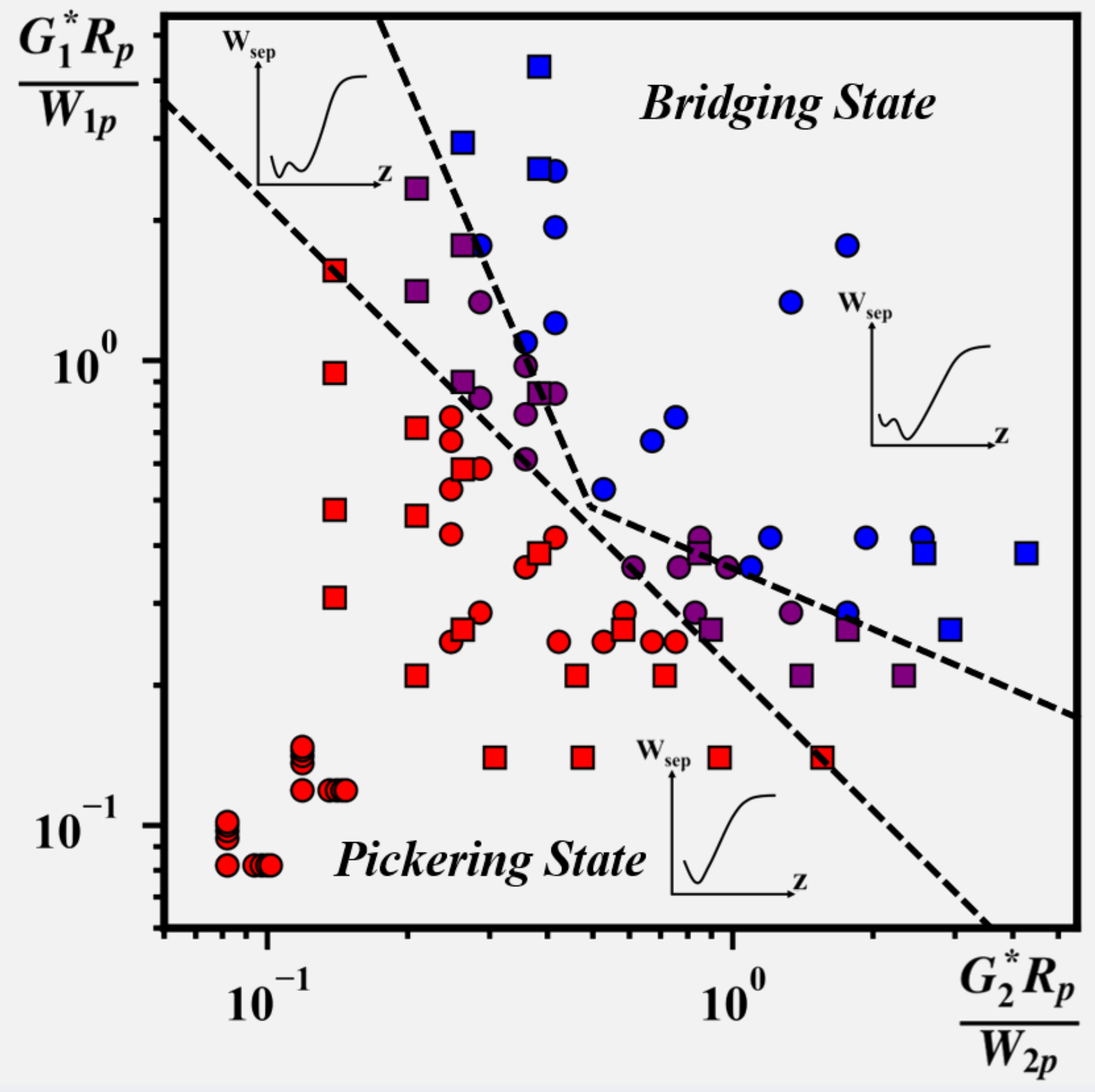
Universality



W_{12}: Work of separation between two gels without interface reinforcement

Symmetry of Contact





Rigid Nanoparticles

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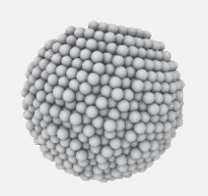

Soft Nanoparticles

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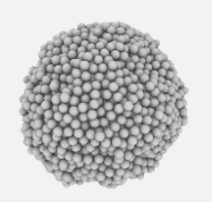

Elastocapillary Length

$$\xi_{el}^i = W_{ip}/G_i^*$$

Effective Modulus

$$G_i^* = \frac{G_iG_p}{G_i + G_p}$$

Conclusion

- **A shape of contact between a nanoparticle and substrates is a result of a fine interplay between elastic and capillary forces.**
- **The Pickering state is more favorable for smaller and softer nanoparticles while the bridging state is more favorable for larger rigid nanoparticles.**
- **In a crossover between Pickering and bridging states, the bridging state is a metastable state.**
- **A universal behavior describing soft and rigid nanoparticle confinement is characterized by the ratio of nanoparticle size to elastocapillary length of nanoparticle/substrate interface.**

References

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