Nanoparticles composed of macroscopically hydrophilic material become hydrophobic on the nanometer length scale

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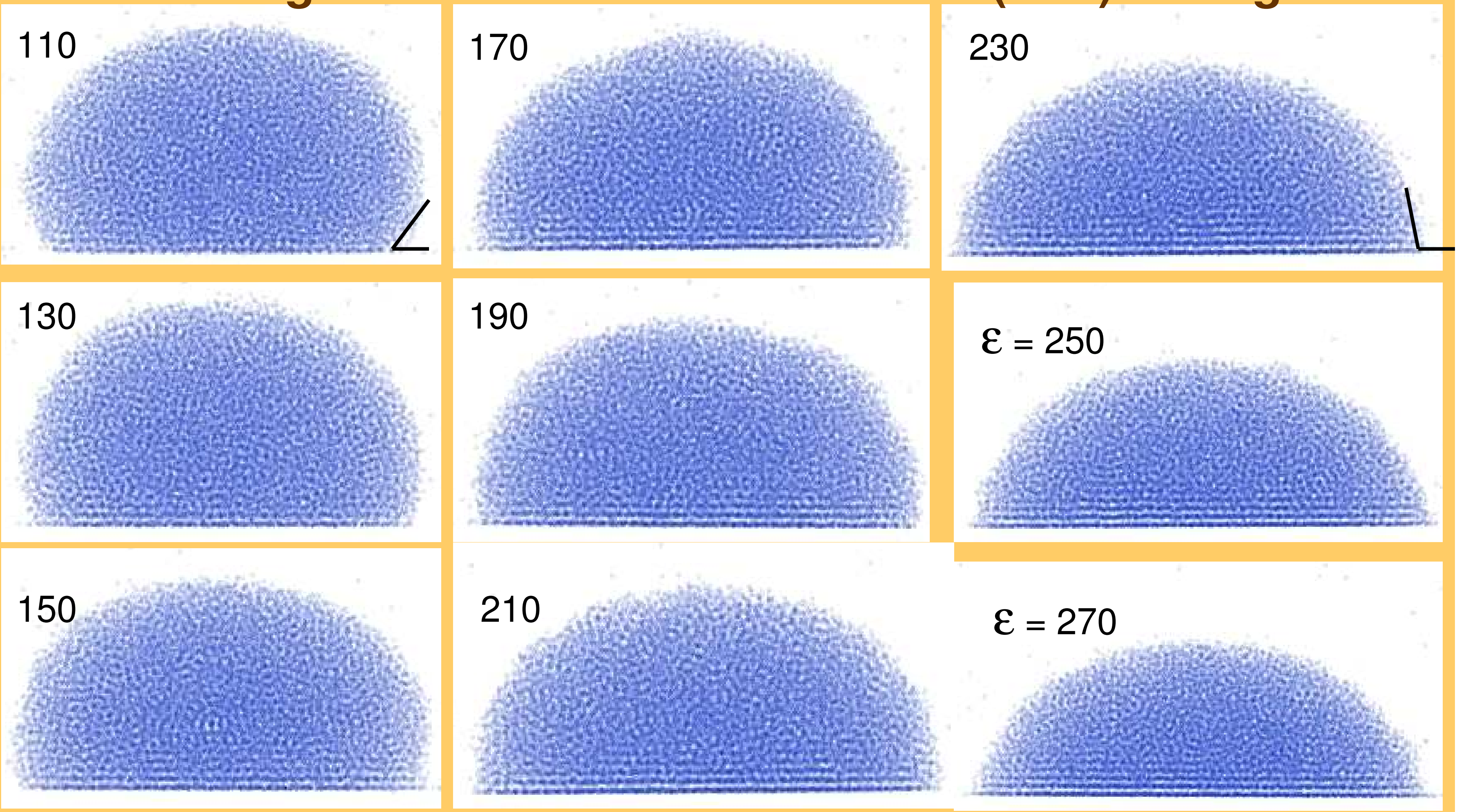
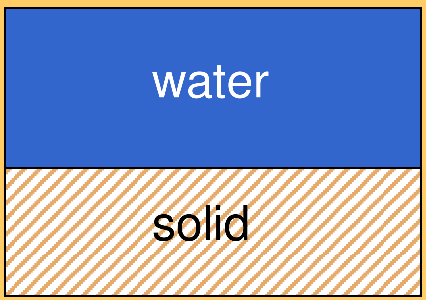
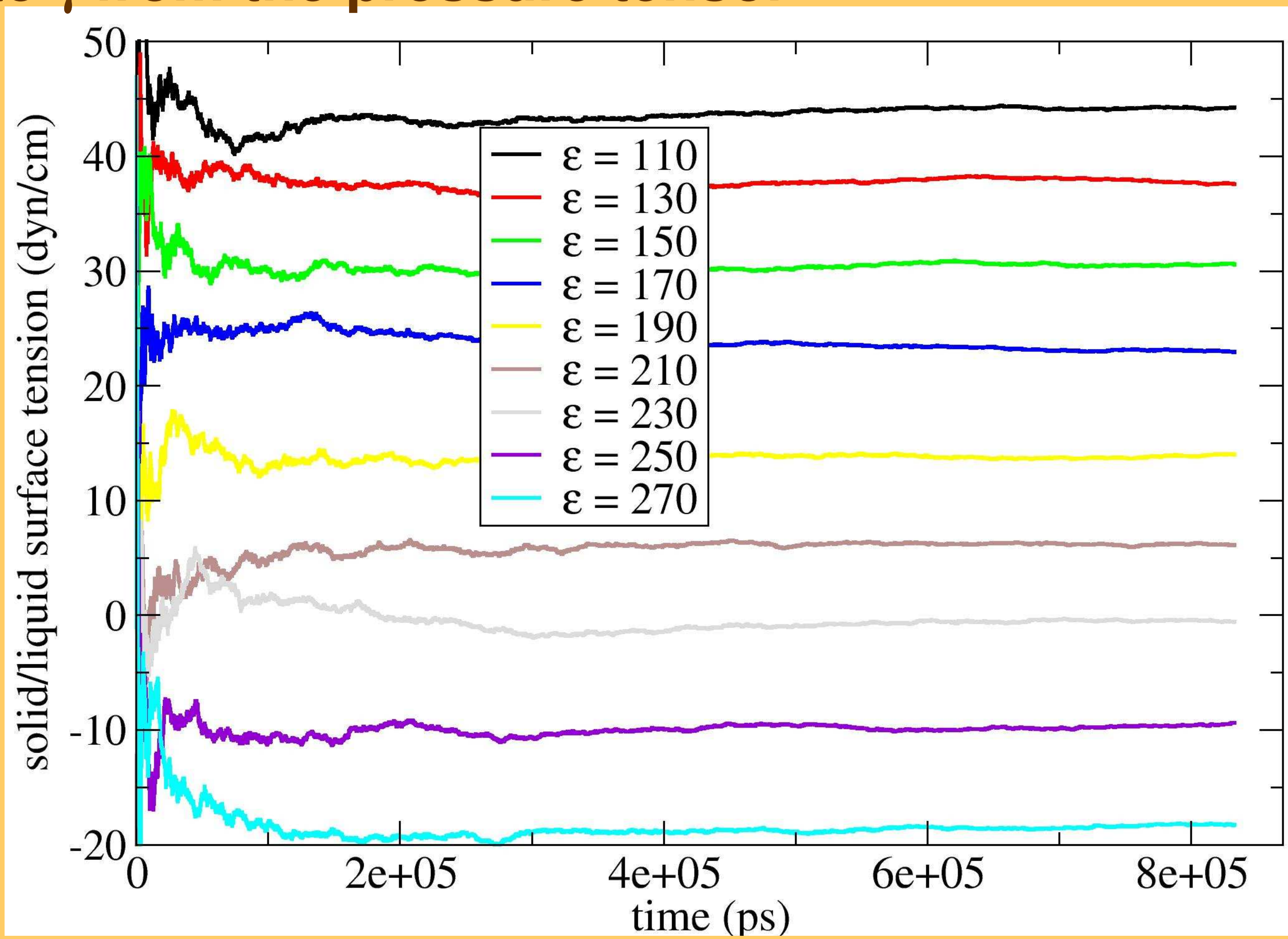
A material is classified as hydrophobic (or hydrophilic) if its contact angle with a bubble of water is < (or >) 90 degrees.



$$water\,/\,solid(z) = 0.0338\varepsilon\sigma^{9}z^{-6} - 0.118\varepsilon\sigma^{6}z^{-3}$$

The surface tension, γ, can be calculated from the cosine of the angle. An independent method for measuring γ is to simulate a slab of water and evaluate γ from the pressure tensor.

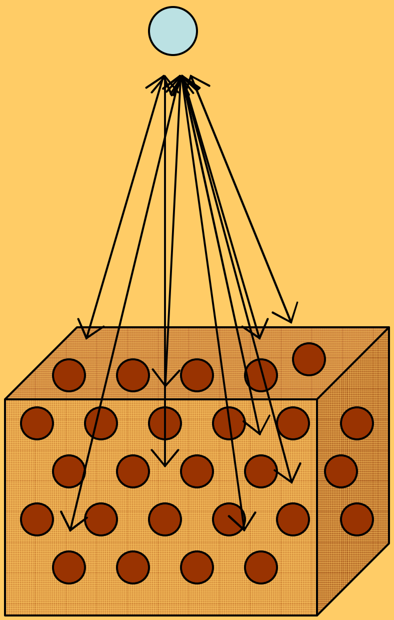


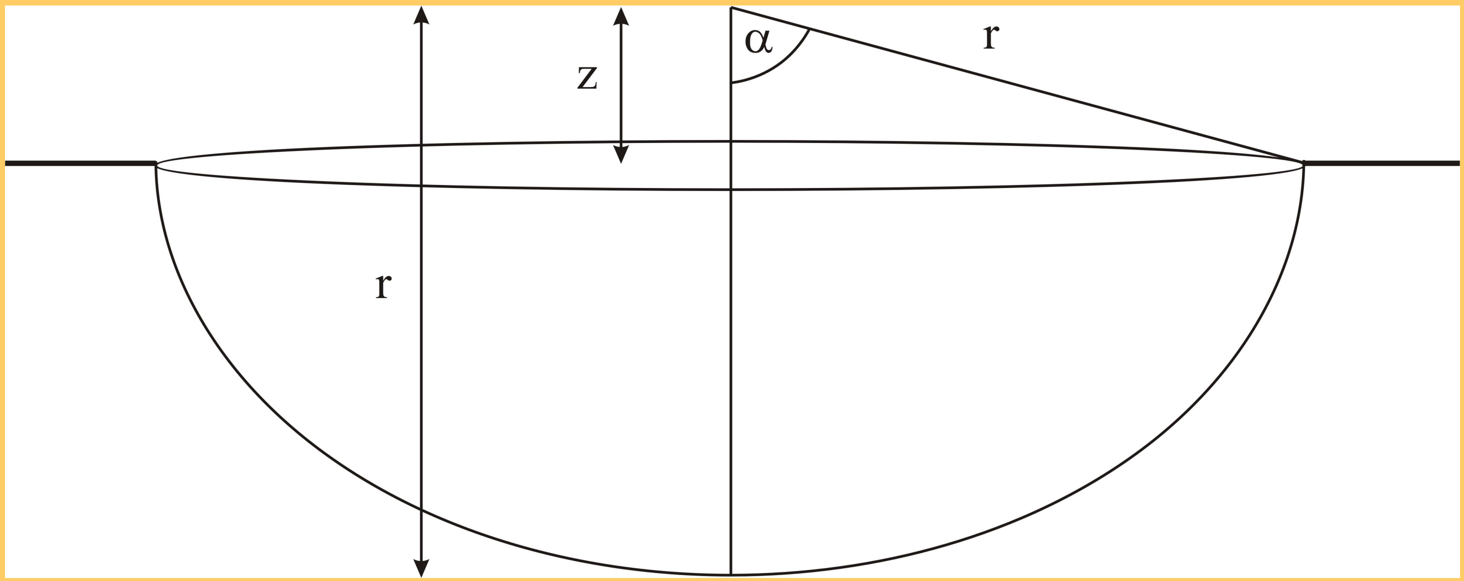


$$water/solid(z) = 0.0338\varepsilon\sigma^{9} z^{-6} - 0.118\varepsilon\sigma^{6} z^{-3}$$

Where does the solid/water potential come from? We integrate the site-site potential over the solid slab

Approximate the solid as a continuum with number density $\rho = N/V$ that occupies the semi-infinite region $z < 0$





Spherical shell of radius r below z = 0. **$\cos\alpha = z/r$**

$$\int_z^\infty dr \int_0^{2\pi} d\theta \int_{\pi-\cos^{-1}(z/r)}^{\pi} d\phi \, \underbrace{r^2 \sin\phi}_{\text{Jacobian}} \, \rho \, u(r) = 2\pi\rho \int_z^\infty r\, u(r)[r-z]dr$$

$$= \frac{4}{45}\frac{\pi\rho\epsilon\sigma^{12}}{z^9} - \frac{2}{3}\frac{\pi\rho\epsilon\sigma^6}{z^3} = U(z)$$

Density of carbon atoms in graphite:

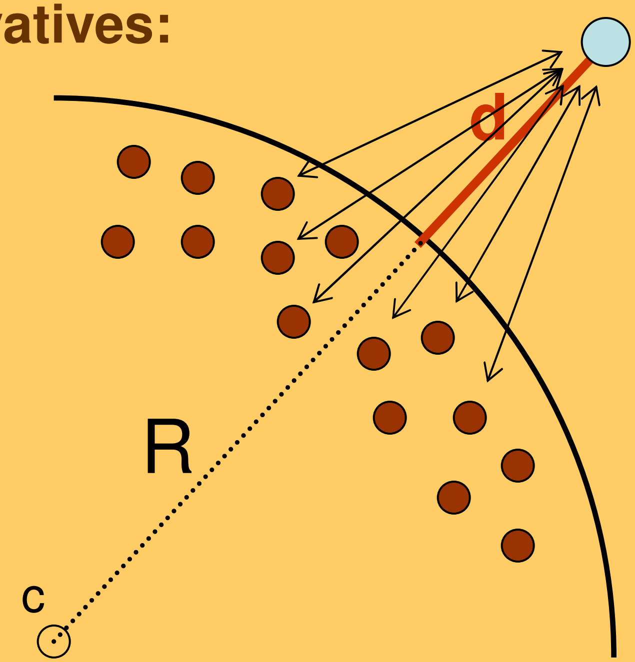
$$\rho = 0.113 \text{ Å}^{-3}$$

(1.42 in-plane bond length and 3.4 inter-layer spacing)

How do we curve the solid into a sphere?

$U(z) = 2\pi\rho \int_z^\infty r\,u(r)[r-z]\,dr$ **yields a relationship that allows us to invert the slab potential U(r) back to the site-site potential u(r) by taking two derivatives:**

$$u(\xi) = \frac{U''(\xi)}{2\pi\rho\xi}$$

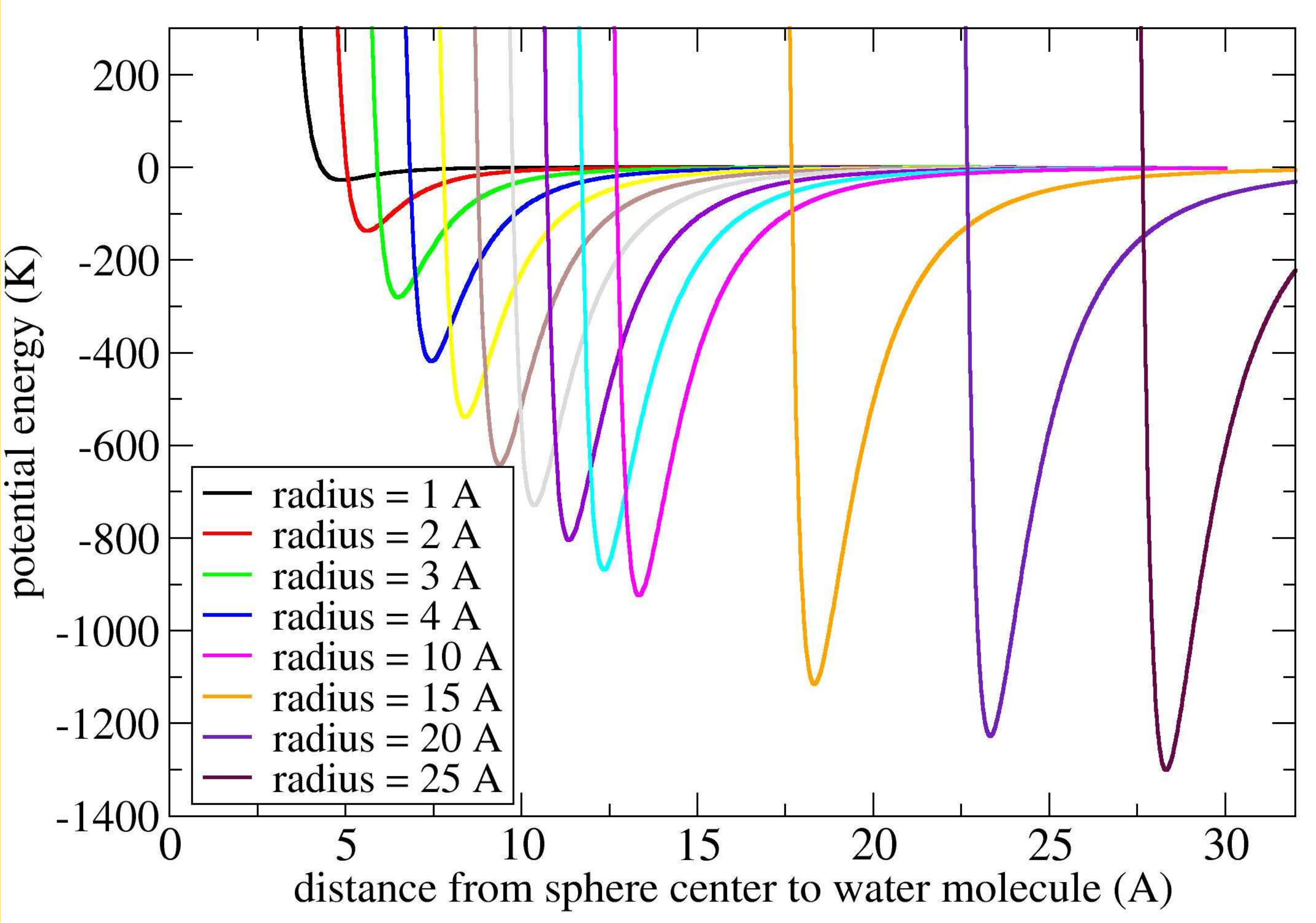


Then we can integrate the site-site potential u(r) over a spherical solid as:

$$U(d,R) = \int_0^R dr \int_0^{2\pi} d\theta \int_0^\pi d\phi\, \rho r^2 \sin\phi\, u([r^2 + (d+R)^2 - 2r\cos\phi(d+R)]^{1/2})$$

$$U(d,R) = \frac{4a\varepsilon\sigma^9 R^3}{5d^6} \cdot \frac{35d^4 + 140Rd^3 + 252R^2d^2 + 224R^3d + 80R^4}{(d+R)(d+2R)^6} - \frac{8b\varepsilon\sigma^6 R^3}{d^3(d+2R)^3}$$

This potential energy function looks like (for Ɛ = 250, hydrophilic):

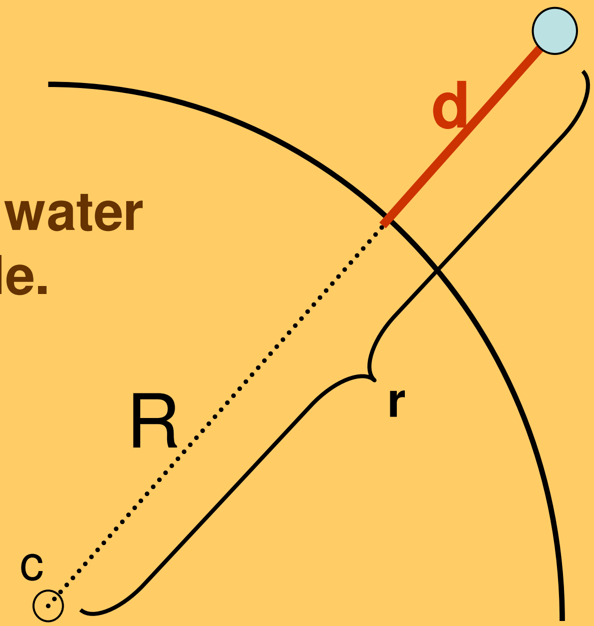


The well depth converges to the flat geometry (slab) potential.

Change variables from U(d,R) to U(r,R).

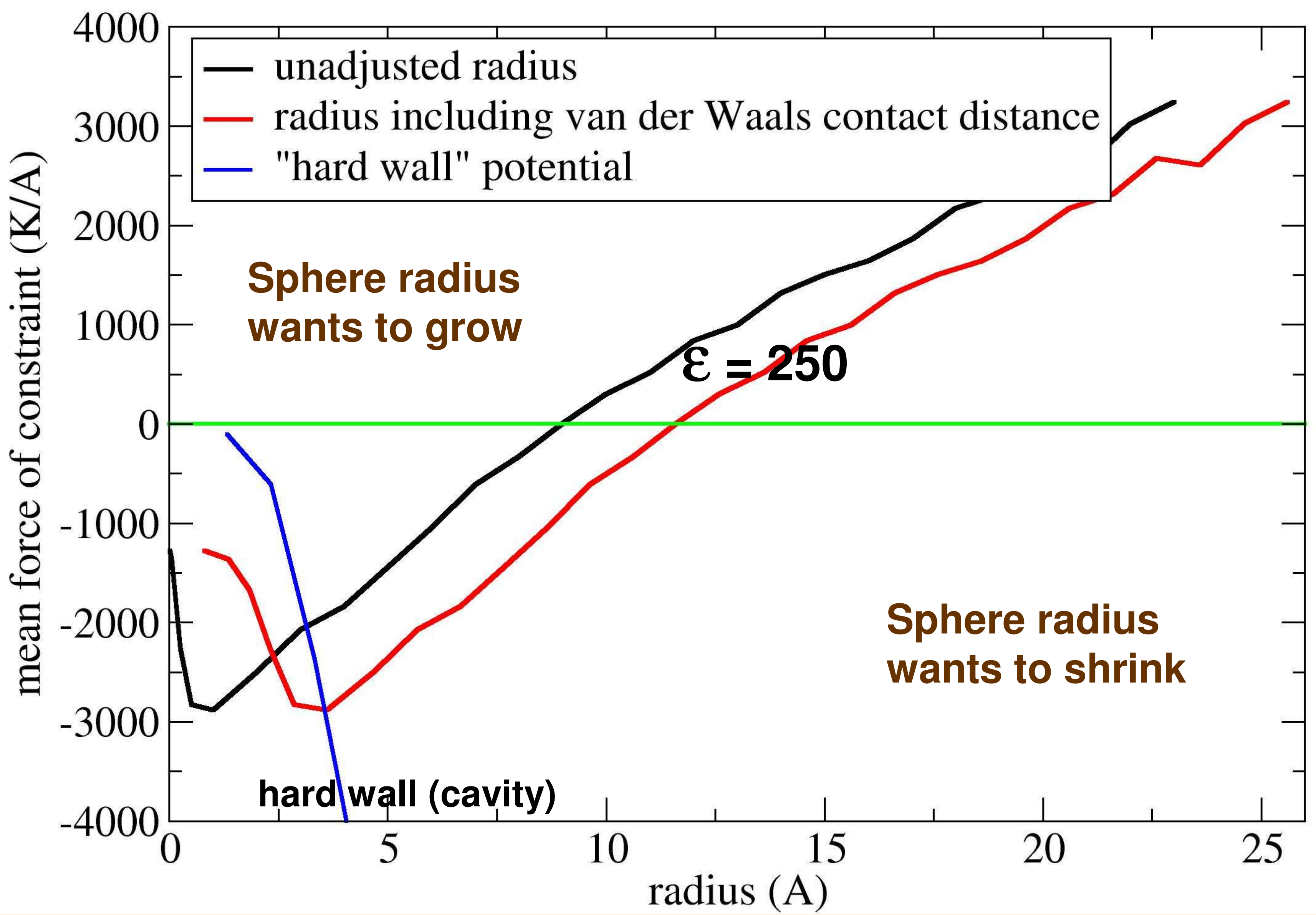
Then $\pm\dfrac{\partial U}{\partial r}$ gives the usual MD force on the water molecule and on the nanoparticle.

What about $-\dfrac{\partial U}{\partial R}$? This is the force on the sphere radius, which we don't use since it is fixed.

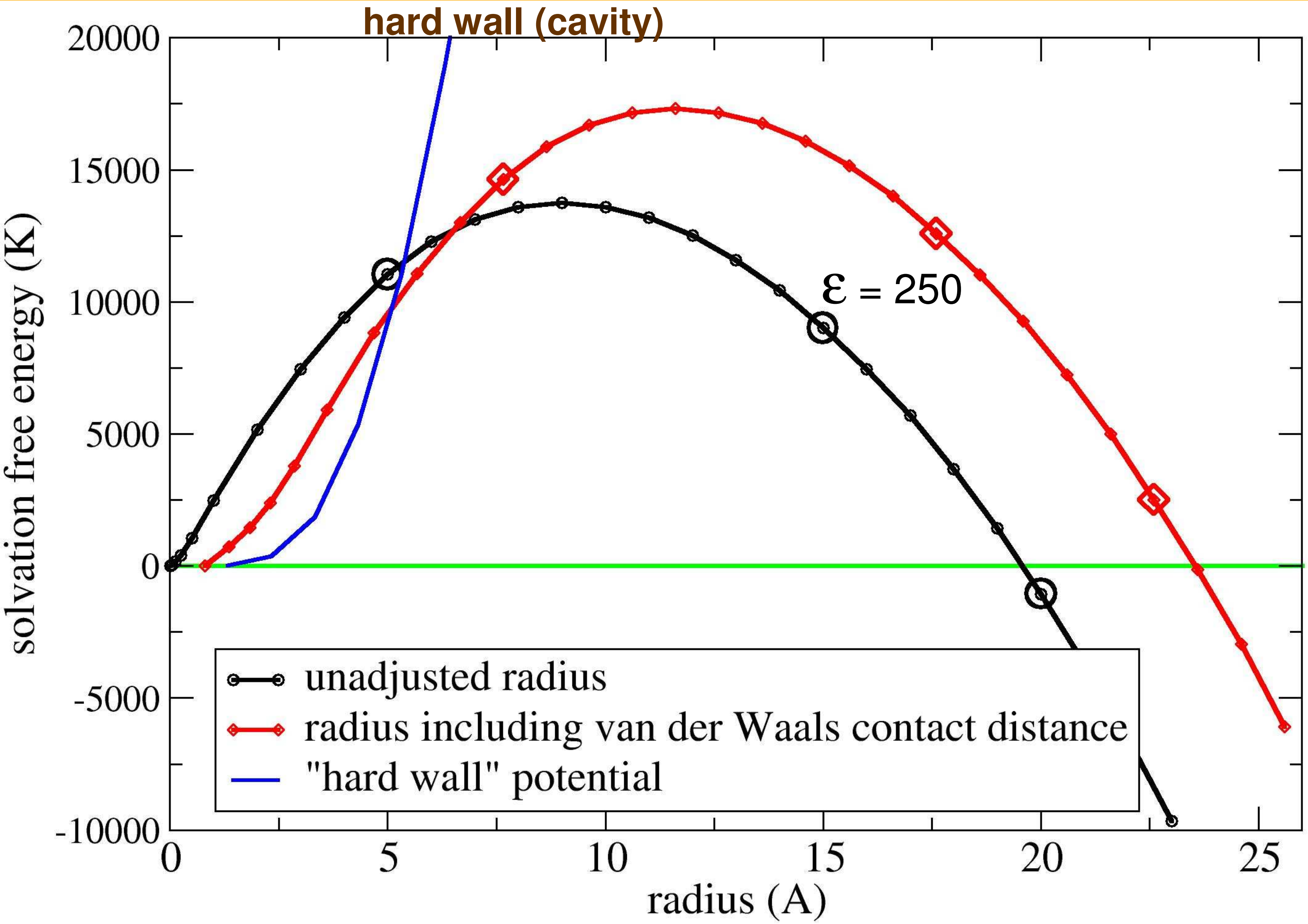


However, if we keep track of it during the MD simulation we obtain a powerful quantity to use to calculate free energy.

Simulations of a fixed radius sphere in water: measure the force on the sphere radius.



Integrate to obtain the solvation free energy of a sphere of radius R.



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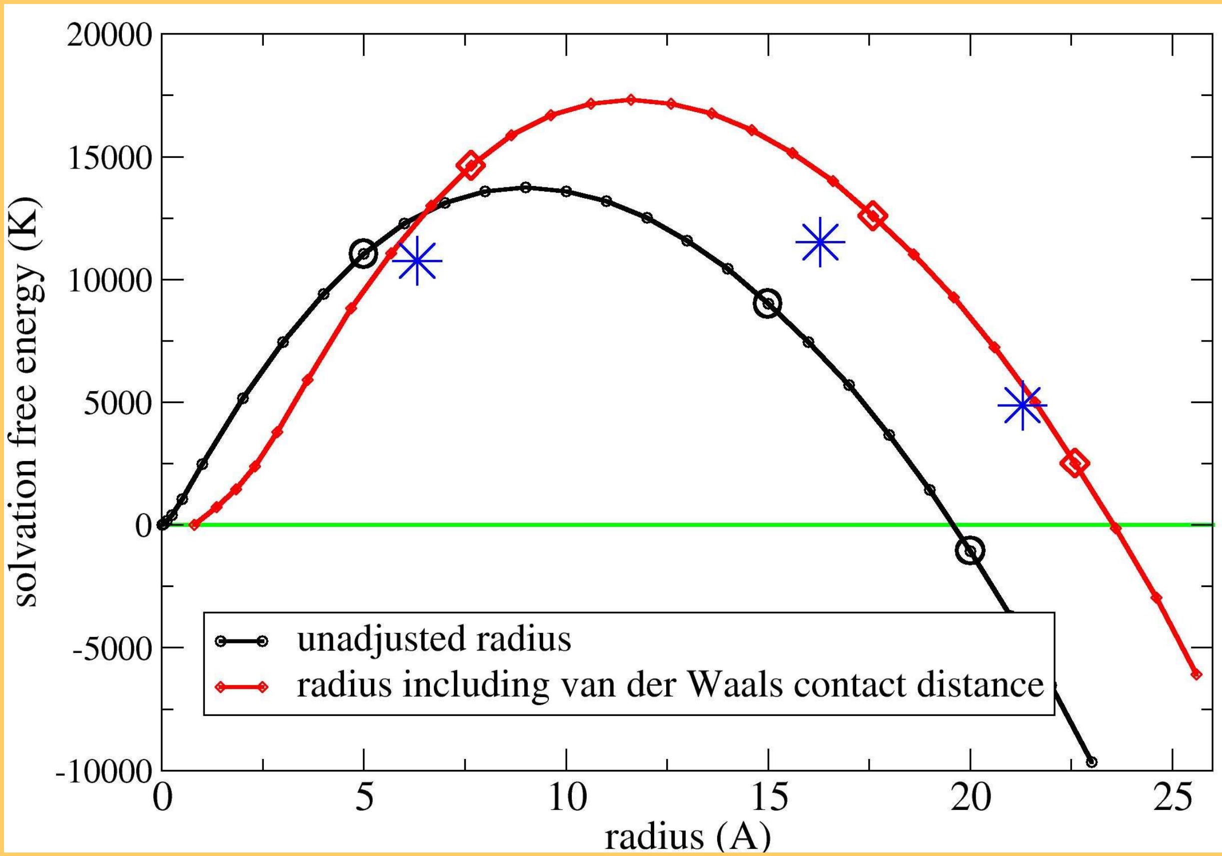
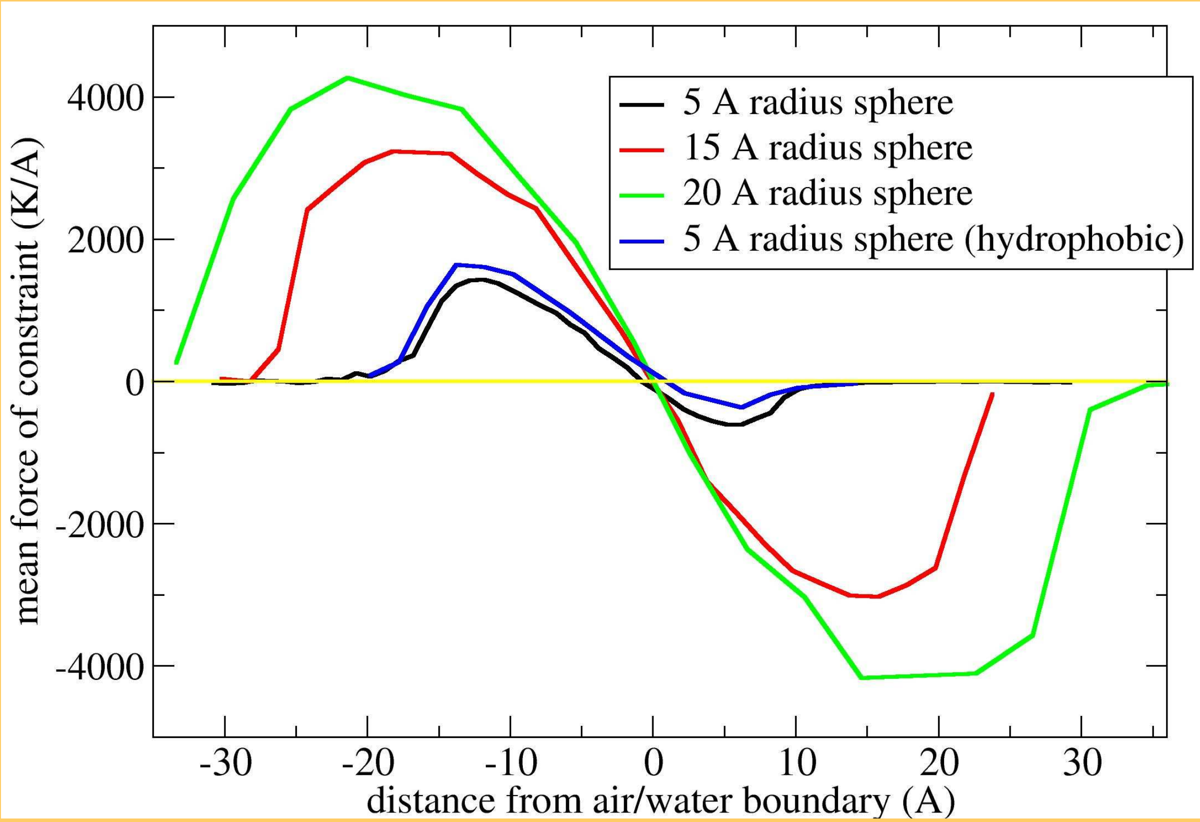
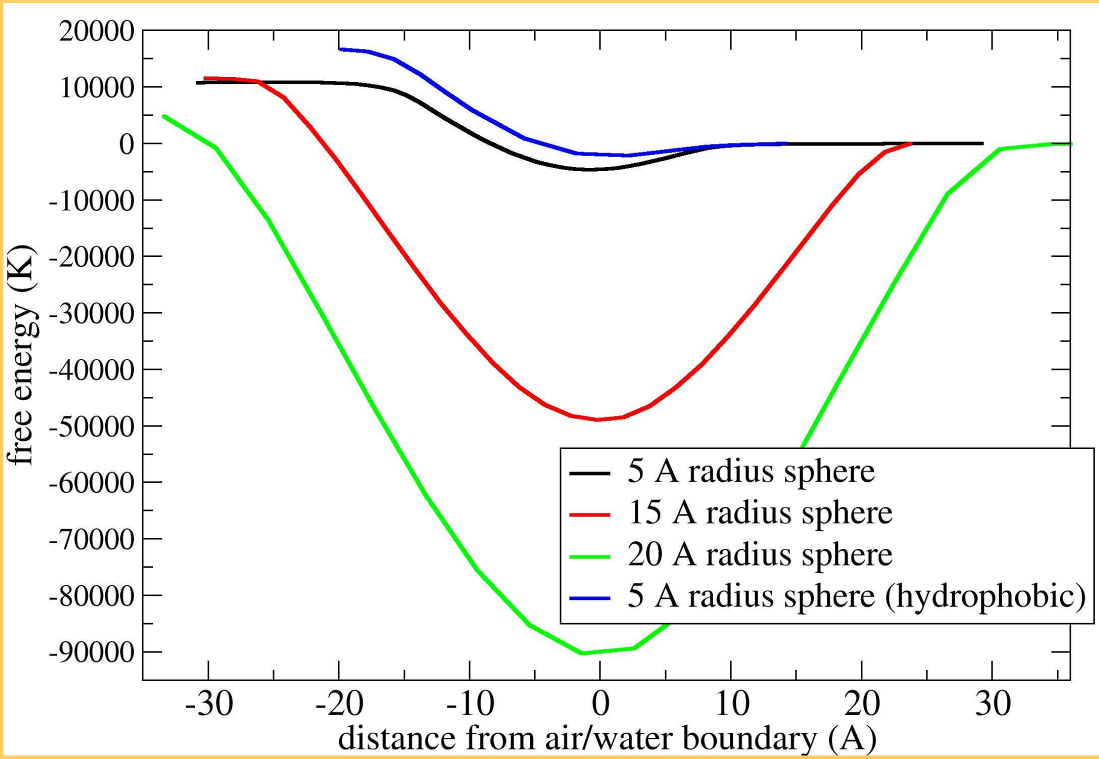


20000
15000
10000
5000
0
-5000
-10000
0
5
10
15
20
25
solvation free energy (K)
radius (A)
unadjusted radius
radius including van der Waals contact distance



5 A radius sphere
15 A radius sphere
20 A radius sphere
5 A radius sphere (hydrophobic)
mean force of constraint (K/A)
4000
2000
0
-2000
-4000
-30
-20
-10
0
10
20
30
distance from air/water boundary (A)



free energy (K)
distance from air/water boundary (A)
5 A radius sphere
15 A radius sphere
20 A radius sphere
5 A radius sphere (hydrophobic)