

Mirror Charges, Hydrogen Bonds, And the Water-Dielectric Interface

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Field Energy

The energy E of an electric field $\mathbf{E}(\vec{x}, t)$ is the space integral of its square:

$$E = \frac{1}{8\pi} \int d^3x \mathbf{E}^2(x, t). \quad (1)$$

In a medium with a high dielectric constant ϵ , electric fields are screened. So the field energy of a charge in water ($\epsilon \approx 80$) is much less than in air ($\epsilon \approx 1$) or in a hydrophobic dielectric ($\epsilon \approx 2$).

Thus as a charge or an electric dipole in water approaches an interface with protein (or wax), the electric field lines of the charge extend into the protein with less damping than in water. As the field energy in the protein rises, the charge is repelled from the protein-water interface.

The rest of this talk is about this simple idea.

Mirror Charges

A mirror charge is a standard, simple trick for computing the energy of a charge q near an interface between two dielectrics.

Let ϵ_w stand for the dielectric constant of water, and ϵ_d be the dielectric constant of the dielectric (e.g., protein or wax).

Let's take the interface to be the plane $z = 0$, with the water above the dielectric. In the water, Gauss's law reads

$$\epsilon_w \nabla \cdot \mathbf{E} = 4\pi\rho \quad z > 0 \quad (2)$$

where ρ is the charge density. In the dielectric, there is no free charge, and Gauss's law says

$$\epsilon_d \nabla \cdot \mathbf{E} = 0 \quad z < 0. \quad (3)$$

We ignore any time dependence, and so the curl of the electric field vanishes:

$$\nabla \times \mathbf{E} = 0 \quad \text{everywhere.} \quad (4)$$

Boundary Conditions

The boundary conditions at $z = 0$ are

$$\epsilon_w E_z(\rho, \phi, \delta) = \epsilon_d E_z(\rho, \phi, -\delta) \quad (5)$$

$$E_x(\rho, \phi, \delta) = E_x(\rho, \phi, -\delta) \quad (6)$$

$$E_y(\rho, \phi, \delta) = E_y(\rho, \phi, -\delta). \quad (7)$$

as $\delta \rightarrow 0$.

These boundary conditions are linear in the electric fields, as are the field equations (2--4), which express Gauss's law.

Since $\nabla \times \mathbf{E} = 0$ everywhere, the electric field \mathbf{E} is the gradient of an electrostatic potential Φ ,

$$\mathbf{E} = -\nabla \Phi. \quad (8)$$

The Mirror-Charge Trick

If we had only a charge q at $(0, 0, z_0)$ in water and no other dielectric, then the electrostatic potential Φ at the point (ρ, ϕ, z) would be

$$\Phi = \frac{1}{\epsilon_w} \frac{q}{R_w} \quad (9)$$

where $R_w = \sqrt{\rho^2 + (z - z_0)^2}$.

The mirror-charge trick is to put a fake “mirror charge” q' at the point $(0, 0, -z_0)$.

The electrostatic potential Φ at the point (ρ, ϕ, z) in the water now is

$$\Phi = \frac{1}{\epsilon_w} \left(\frac{q}{R_w} + \frac{q'}{R_d} \right) \quad (10)$$

where $R_d = \sqrt{\rho^2 + (z + z_0)^2}$, while in the dielectric it is

$$\Phi = \frac{1}{\epsilon_d} \frac{q''}{R_w}. \quad (11)$$

What Are q' and q'' ?

The linear field equations and the boundary conditions tell us that the charges q' and q'' are proportional to the physical charge q . In particular, the image charge q' is

$$q' = \left(\frac{\epsilon_w - \epsilon_d}{\epsilon_w + \epsilon_d} \right) q. \quad (12)$$

If $\epsilon_w = 80$, and $\epsilon_d = 2$, then $\epsilon_w > \epsilon_d$, and so the image charge has the same sign as the real charge q . In fact, $q' \approx q$.

So the physical charge is repelled by the dielectric interface in agreement with our initial intuition about the energy of electric fields --- unless, of course, the dielectric is a metal with $\epsilon_d > 80$.

The electrostatic potential seen by the real charge q is

$$\Phi = \frac{1}{\epsilon_w} \frac{q'}{R_d} = \frac{1}{\epsilon_w} \frac{q'}{2r} = \frac{1}{\epsilon_w} \left(\frac{\epsilon_w - \epsilon_d}{\epsilon_w + \epsilon_d} \right) \frac{q}{2z_0}. \quad (13)$$

Energy of Charge near Interface

So in the field of the image charge q' , the energy H_q of a real charge q at the point $(0, 0, z)$ (we are using z for z_0) is

$$H_q(z) = \Phi q = \frac{1}{\epsilon_w} \left(\frac{\epsilon_w - \epsilon_d}{\epsilon_w + \epsilon_d} \right) \frac{q^2}{2z}. \quad (14)$$

The repulsive force F on the real charge q is in the positive z -direction

$$F = -\frac{\partial}{\partial z} H_q(z) = \frac{1}{\epsilon_w} \left(\frac{\epsilon_w - \epsilon_d}{\epsilon_w + \epsilon_d} \right) \frac{q^2}{2z^2}. \quad (15)$$

Note that the force falls off as $1/z^2$. The force on an electric dipole falls off much faster, as $1/z^4$.

So at long distances, an ion exerts a greater force on a dielectric than does a dipole.

Electric Dipoles

Because the field equations and the boundary conditions are linear, we can apply the mirror-charge trick to the case of two equal and opposite charges q and $-q$ at the points $\mathbf{r}_+ = (p \sin \theta, 0, z + p \cos \theta)$ and $\mathbf{r}_- = (-p \sin \theta, 0, z - p \cos \theta)$. The distance between the charges is $2p$. The angle between the normal to the interface and the vector $\mathbf{r}_+ - \mathbf{r}_-$ is θ .

There are now two image charges. The charge

$$q' = \left(\frac{\epsilon_w - \epsilon_d}{\epsilon_w + \epsilon_d} \right) q \quad (16)$$

is at $\mathbf{r}'_+ = (p \sin \theta, 0, -(z + p \cos \theta))$, and the charge $-q'$ is at the point $\mathbf{r}'_- = (-p \sin \theta, 0, -z + p \cos \theta)$.

The two image charges make the potential

$$\Phi(\mathbf{r}) = \frac{q'}{\epsilon_w} \left(\frac{1}{|\mathbf{r} - \mathbf{r}'_+|} - \frac{1}{|\mathbf{r} - \mathbf{r}'_-|} \right) \quad (17)$$

at the point \mathbf{r} in the water ($z > 0$).

Energy of an Electric Dipole

Thus the energy of the electric dipole is

$$H_d = q (\Phi(\mathbf{r}_+) - \Phi(\mathbf{r}_-)) \quad (18)$$

or

$$H_d = \frac{q^2}{\epsilon_w} \left(\frac{\epsilon_w - \epsilon_d}{\epsilon_w + \epsilon_d} \right) \left(\frac{1}{|\mathbf{r}_+ - \mathbf{r}'_+|} - \frac{1}{|\mathbf{r}_+ - \mathbf{r}'_-|} - \frac{1}{|\mathbf{r}_- - \mathbf{r}'_+|} + \frac{1}{|\mathbf{r}_- - \mathbf{r}'_-|} \right) \quad (19)$$

or

$$H_d(z, \theta) = \frac{q^2}{\epsilon_w} \left(\frac{\epsilon_w - \epsilon_d}{\epsilon_w + \epsilon_d} \right) \left(\frac{z}{z^2 - p^2 \cos^2 \theta} - \frac{1}{\sqrt{z^2 + p^2 \sin^2 \theta}} \right). \quad (20)$$

This energy H_d has a minimum at $\theta = \pi/2$ and maxima at $\theta = 0$ and $\theta = \pi$. It is big at short distances.

We resist the urge to expand it in inverse powers of $1/z$ because long-distance expansions fail at short distances.

Surface Energy of Interface

The probability that an ion or a dipole will be at a distance z from the interface is proportional to

$$\exp(-H/(kT)). \quad (21)$$

The interface is dry, because as $z \rightarrow 0$, $H_q(z) \rightarrow \infty$ and $H_d(z, \theta) \rightarrow \infty$.

As a real interface has a finite extent D , we count monopole and dipole energies only out to a distance L comparable to D . So the energy associated with an interface of cross-sectional area A due to a density ρ of charges or of dipoles is

$$E = \rho A L \frac{\int_0^L dz \int_0^\pi \sin \theta d\theta H(z, \theta) e^{-H(z, \theta)/(kT)}}{\int_0^L dz \int_0^\pi \sin \theta d\theta e^{-H(z, \theta)/(kT)}} \quad (22)$$

where $H = H_q$ or $H = H_d$. The energy per unit area is

$$\sigma = \rho L \frac{\int_0^L dz \int_0^\pi \sin \theta d\theta H(z, \theta) e^{-H(z, \theta)/(kT)}}{\int_0^L dz \int_0^\pi \sin \theta d\theta e^{-H(z, \theta)/(kT)}}. \quad (23)$$

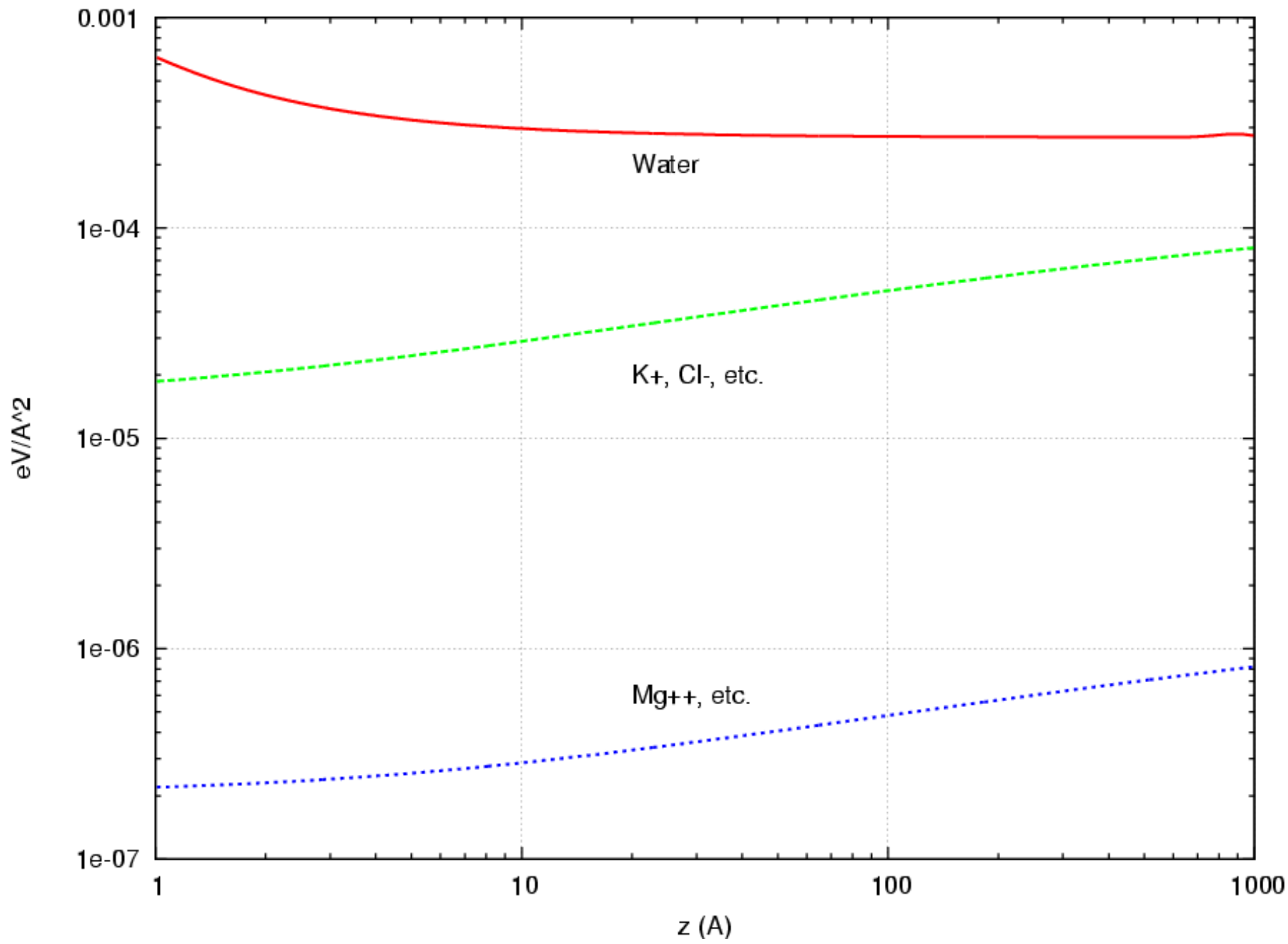
Mammalian Cells

In a typical mammalian cell, the concentration (mM) of free ions is about 140 for K^+ , 10 for Na^+ , 10 for Cl^- , 140 for HCO_3^- and other negatively charged molecules taken together, and 0.5 for Mg^{++} . (The concentration of Mg^{++} bound to proteins, etc., is about 20 mM.) Pure water is about 55 M.

The next slide shows the surface energy σ of Eq.(23) in units of $eV/\text{\AA}^2$ for values of the length cutoff $L \equiv z$ ranging from 1 to 10^3\AA .

Since globular proteins are between 30 and 100 \AA in diameter, a length cutoff L in the range of 10--30 \AA seems about right. For that range of L , and for $p = 0.36\text{\AA}$ and a dipole moment of $2p(0.8)e = 0.58 e\text{\AA}$ for water, the total surface energy σ is 0.3 meV per \AA^2 or 6.9 cal/(\AA^2 mol).

The surface energy due to ions adds about 0.03 meV per \AA^2 .



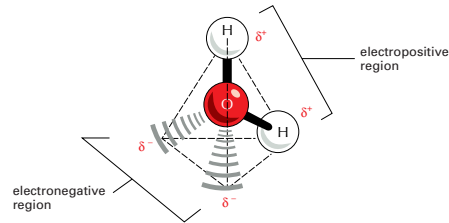
Frustrated Hydrogen Bonds

But water molecules near a large protein molecule can't form all four of the hydrogen bonds that they normally form with other water molecules. Each frustrated hydrogen bond costs an energy of about 1 kcal/mol or $E_H = 0.04336$ eV per molecule.

PANEL 2-2 Water and Its Influence on the Behavior of Biological Molecules

WATER

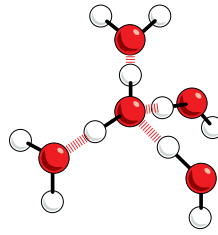
Two atoms, connected by a covalent bond, may exert different attractions for the electrons of the bond. In such cases the bond is **polar**, with one end slightly negatively charged (δ^-) and the other slightly positively charged (δ^+).



Although a water molecule has an overall neutral charge (having the same number of electrons and protons), the electrons are asymmetrically distributed, which makes the molecule polar. The oxygen nucleus draws electrons away from the hydrogen nuclei, leaving these nuclei with a small net positive charge. The excess of electron density on the oxygen atom creates weakly negative regions at the other two corners of an imaginary tetrahedron.

WATER STRUCTURE

Molecules of water join together transiently in a hydrogen-bonded lattice. Even at 37°C, 15% of the water molecules are joined to four others in a short-lived assembly known as a "flickering cluster."

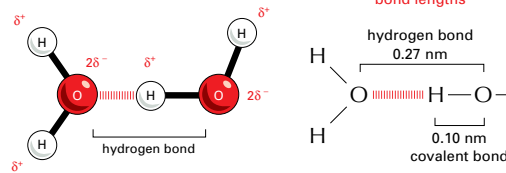


The cohesive nature of water is responsible for many of its unusual properties, such as high surface tension, specific heat, and heat of vaporization.

HYDROGEN BONDS

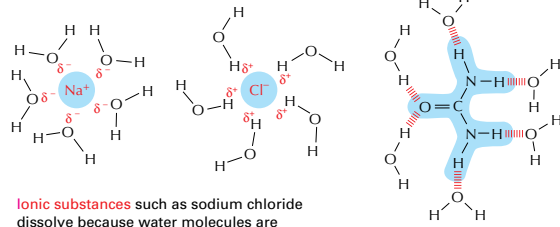
Because they are polarized, two adjacent H₂O molecules can form a linkage known as a **hydrogen bond**. Hydrogen bonds have only about 1/20 the strength of a covalent bond.

Hydrogen bonds are strongest when the three atoms lie in a straight line.



HYDROPHILIC MOLECULES

Substances that dissolve readily in water are termed **hydrophilic**. They are composed of ions or polar molecules that attract water molecules through electrical charge effects. Water molecules surround each ion or polar molecule on the surface of a solid substance and carry it into solution.

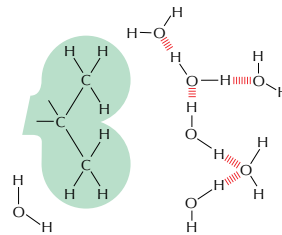


Ionic substances such as sodium chloride dissolve because water molecules are attracted to the positive (Na⁺) or negative (Cl⁻) charge of each ion.

Polar substances such as urea dissolve because their molecules form hydrogen bonds with the surrounding water molecules.

HYDROPHOBIC MOLECULES

Molecules that contain a preponderance of non-polar bonds are usually insoluble in water and are termed **hydrophobic**. This is true, especially, of hydrocarbons, which contain many C-H bonds. Water molecules are not attracted to such molecules and so have little tendency to surround them and carry them into solution.



Energy of Frustrated Hydrogen Bonds

The density ρ of water is 0.0334 molecules per \AA^3 . Let's allow $t = \rho^{-1/3} = 3.1\text{\AA}$ as the thickness of the layer of water molecules with frustrated H-bonds. Suppose 7 out of 10 of these bonds actually are frustrated. Then the surface energy σ_H due to the frustrated H-bonds is

$$\sigma_H = 0.7 \rho t E_H = 3.15 \text{ meV} \quad (24)$$

per \AA^2 . So the sum of these surface energies gives a surface energy $\sigma_W = \sigma + \sigma_H = 3.45 \text{ meV}\text{\AA}^{-2}$ or about $80 \text{ cal}\text{\AA}^{-2}/\text{mol}$ for the protein-water interface. The experimental value is $75 \text{ cal}\text{\AA}^{-2}\text{mol}^{-1}$, so we overestimated something.

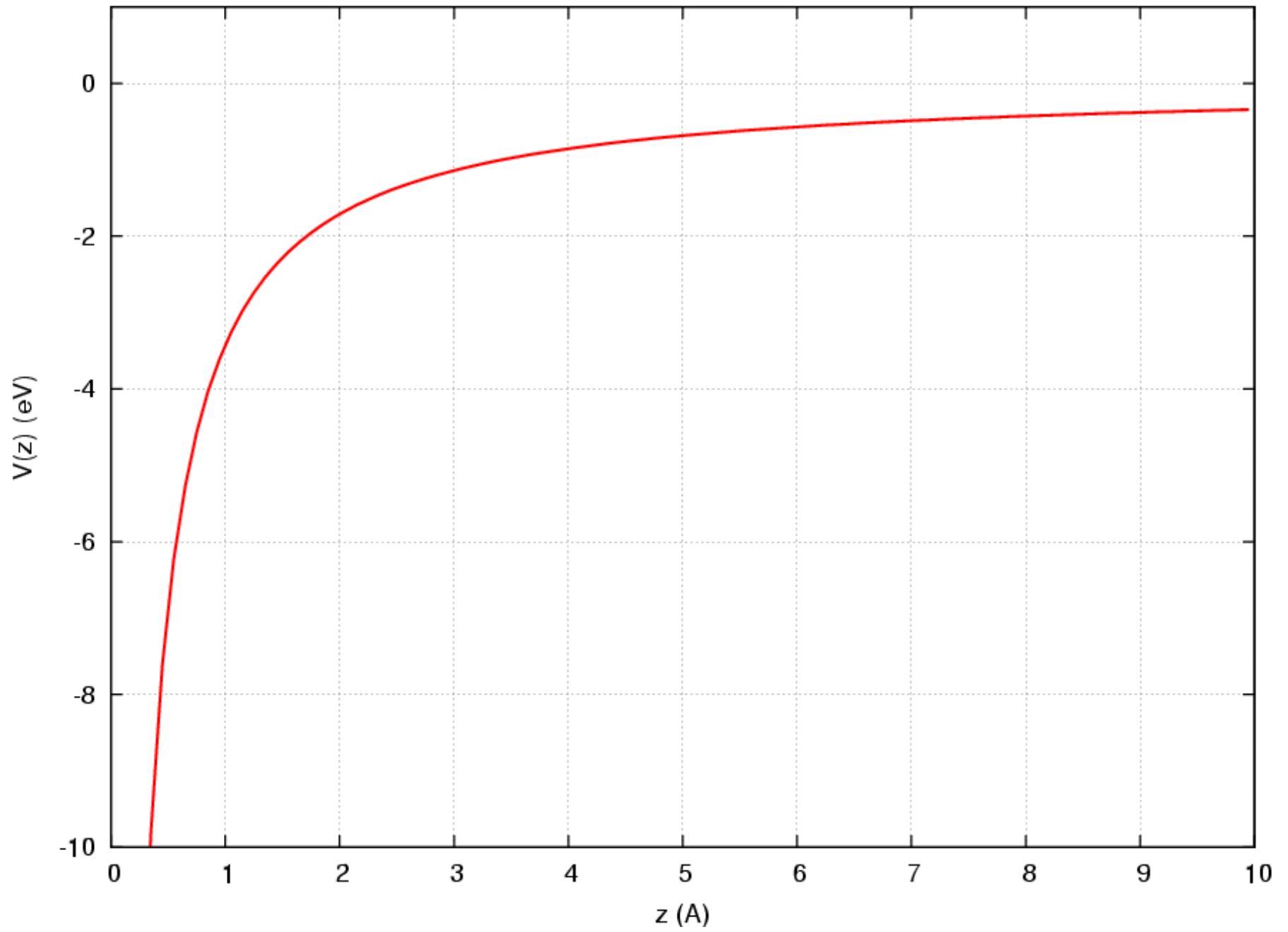
A protein of diameter d has a surface energy $E = \pi d^2 \sigma_T$. Using $\sigma_T = 3.3 \text{ meV}$ for the surface energy including ions, we find that for $d = 30\text{\AA}$, the surface energy is 9.33 eV or 215 kcal/mol . For $d = 100\text{\AA}$, it is 104 eV or 2391 kcal/mol .

What about a Charge Buried in a Protein?

A charge buried inside a protein near a relatively flat interface feels a potential energy $V(z)$ given by Eq.(14) with ϵ_w and ϵ_d interchanged:

$$V(z) = -\frac{1}{\epsilon_d} \left(\frac{\epsilon_w - \epsilon_d}{\epsilon_w + \epsilon_d} \right) \frac{q^2}{2z}. \quad (25)$$

This potential energy is plotted in the next slide out to 10 Å for a unit charge. It drops from about -0.34 eV (-7.9 kcal/mol) at 10 Å to about -1.7 eV or (-39 kcal/mol) at 2 Å.



Conclusions

Programs that search for low-energy states of macromolecules should take into account a surface energy σ of the order of 75 cal per \AA^2 per mol. This surface term represents the hydrophobic effect.

Search programs also should include potential-energy terms like $V(z)$ that push buried charges to the surfaces of macromolecules.