Elementary theories of solvation

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These are some some notes on the most simple approaches to solvation, in terms of classical electrostatics. For some reason I have had trouble finding suitable sources of information on this subject, perhaps because it is widely assumed to already be common knowledge by most authors.

Suggestions or mistakes sent to my email would be greatly appreciated.

1 Free energy of a charge distribution in a dielectric media

Consider a continuous charge distribution in a dielectric medium, producing a potential ϕ. Now consider the work necessary to increase the charge density uniformly throughout the distribution by $\delta\rho$. Since the potential depends linearly on the charge density, the change in energy of the system (ie. the work) to a small perturbation is :

$$\delta W = \int_V \phi(\boldsymbol{r})\delta\rho dV \tag{1}$$

In a dielectric, Gauss's law is $\nabla \cdot \boldsymbol{D} = \rho$. Therefore

$$\delta\rho = \nabla \cdot \delta\boldsymbol{D} = \nabla \cdot (\phi\delta\boldsymbol{D}) - \delta\boldsymbol{D} \cdot \nabla\phi \tag{2}$$

where we used the vector identity $\delta \cdot (\phi\boldsymbol{A}) = \delta\phi(\boldsymbol{A}) + \phi\delta \cdot \boldsymbol{A}$. Therefore:

$$\delta W = \int_V \nabla \cdot (\phi\delta\boldsymbol{D})dV - \int_V \delta\boldsymbol{D} \cdot \nabla\phi dV \tag{3}$$

The divergence theorem says that the first integral is equal to a surface integral of the gradient. If we expand the volume of integration to infinity then this integral must go to zero, as ϕ will fall at least as fast as $\frac{1}{r}$ for any finite charge distribution. Therefore, only the second integral remains. Substituting $\nabla\phi = \boldsymbol{E}$ we get:

$$\delta W = \int_V \delta\boldsymbol{D} \cdot \boldsymbol{E} \tag{4}$$

At this stage we assume as linear dielectric, so $\delta\boldsymbol{D} = \varepsilon\delta\boldsymbol{E}$. Then for mathematical transparency we parametrize our increase in $\boldsymbol{E}$ by a parameter λ and note that $\delta\boldsymbol{E} = \frac{\partial\boldsymbol{E}}{\partial\lambda}\delta\lambda$ and $\boldsymbol{E} \cdot \delta\boldsymbol{E} = \boldsymbol{E} \cdot \frac{\partial\boldsymbol{E}}{\partial\lambda}\delta\lambda = \frac{1}{2}\frac{\partial E^2}{\partial\lambda}\delta\lambda$ Then we integrate the resulting form from $\boldsymbol{E} = 0$ to $\boldsymbol{E} = \boldsymbol{E}$ to obtain:

$$W = \frac{\varepsilon\epsilon_0}{2}\int_V E^2 dV \tag{5}$$

As is well known, $\frac{E^2}{8\pi}$ is the energy density of an electric field in free space. If ε has any temperature dependence, then in general it is inaccurate to call eqn. 5 the change in energy of the dielectric. The reason for this is that during the derivation we did not specify what thermodynamic changes were happening in the dielectric medium while we were increasing the field or whether we increased the field isothermally or adiabatically. The application of a field has thermodynamic effects, for instance a change in temperature (the electrocaloric effect) or a change in volume (electrostriction) which result in changes to the dielectric constant depending on $\frac{\partial\varepsilon}{\partial T}$ or $\frac{\partial\varepsilon}{\partial P}$. Let's first consider the case where we keep the temperature constant during the application of the field, which is the most common situation in experiments. The first law of thermodynamics says:

$$dU = dQ + dW \tag{6}$$

The second law says that if we make the changes in a reversible fashion, then $dQ = TdS$ and

$$\begin{aligned} dU &= TdS + dW \\ dW &= dU - TdS \end{aligned} \tag{7}$$

If we keep the system at constant volume and temperature, then this change in work is the change in the Helmholtz free energy:

$$\begin{aligned} F &= U - TS \\ dF &= d(U - TS)|_{T,V} = dU - TdS = dW \end{aligned} \tag{8}$$

Thus assuming constant volume and temperature equation 5 is

$$\boxed{\Delta F = \frac{\varepsilon\epsilon_0}{2}\int_V E^2 dV} \tag{9}$$

Using $S = -\left.\frac{\partial F}{\partial T}\right|_{V,D}$ then we can easily derive the following equation for the entropy:

$$\boxed{S = S_0 + \frac{\epsilon_0}{2}\frac{\partial\varepsilon}{\partial T}\int_V E^2 dV} \tag{10}$$

We can also look at the internal energy U by substituting 10 into $U = F + TS$.

$$\begin{aligned} U &= U_0 + \frac{\epsilon_0}{2}\left(\varepsilon + \left(\frac{\partial\varepsilon}{\partial T}\right)T\right)\int_V E^2 dV \\ &= U_0 + \frac{\epsilon_0}{2}\left(\frac{\partial(\varepsilon T)}{\partial T}\right)\int_V E^2 dV \end{aligned} \tag{11}$$

Thus we see that equation 5 refers to the energy only when $\varepsilon \propto \frac{1}{T}$. This is the case for things like dipolar gases, but usually liquids diverge significantly from this behaviour.

Now consider equation 10 for the entropy. In liquids $\frac{\partial\varepsilon}{\partial T}$ is negative, indicating that entropy decreases when the field is applied. Since entropy is a measure of disorder, this means that the field induces order. In some dipolar solids $\frac{\partial\varepsilon}{\partial T}$ is positive, indicating that an external field induces disorder. A change in the slope of $\varepsilon(T)$ sometimes signals a phase change.[1]

2 The simplest model – Born electrostatics + cavity formation

In this section we review the simplest model of solvation, the Born model. Although it is highly naive, the Born model is a natural reference point for more complicated models.

The free energy of solvation can be broken up as:

$$\Delta G = \Delta G_{\text{elec}} + \Delta G_{\text{vdW}} + \Delta G_{\text{cav}} \tag{12}$$

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[1] A notable exception is water, where the dielectric constant anomalously increases during the phase change from liquid to water and then continues to increase with smaller T. This is due to the onset of a proton tunneling contribution to the dielectric constant. In most substances the dielectric constant drops upon freezing and decreases further as T is decreased.

2.1 The Born model

We consider the solute particle to be a sphere of charge Z and radius a embedded in a medium of dielectric constant ε.

The electric field produced by the charge at distances $r > a$ is simply:

$$\boldsymbol{E} = \frac{Z}{4\pi\varepsilon\epsilon_0} \frac{\boldsymbol{r}}{r^3} \tag{13}$$

To find the free energy we use equation 9 and integrate E^2 from $r = a$ to $r = \infty$, yielding:

$$G = \frac{Z^2}{8\pi\varepsilon\epsilon_0 a} \tag{14}$$

Notice how the energy of the system depends on the dielectric constant ε. We can compare the energy of the solute in vacuum $\varepsilon = 1$ with energy in the solvent. This energy difference between these two is the electrostatic contribution to the solvation free energy:

$$\Delta G_{\text{elec}} = \frac{Z^2}{8\pi\epsilon_0 a}\left(\frac{1}{\varepsilon} - 1\right) \tag{15}$$

That is all there is to the Born model. Note that the factor $1 - \frac{1}{\varepsilon} = \chi_L$ appears in the equation.

2.2 Generalized Born

Previously we considered our solute to be spherical, which is a good approximation for single atoms. When considering the solvation of molecules obviously we need to extend Born theory to account for their non-spherical shape. The most obvious extension is to consider each atom in the molecule as a sphere of radius a_i and charge q_i. The electrostatic energy of the molecule is changed as:

$$\Delta G_{\text{elec}} = \sum_{\text{i =1}}^{N} \frac{kq_i^2}{2a_i}\left(\frac{1}{\varepsilon} - 1\right) + \sum_{\text{i, j ¿ i}} \frac{kq_iq_j}{2r_{ij}}\left(\frac{1}{\varepsilon} - 1\right) \tag{16}$$

A common form for f_{GB} is :

$$f_{\text{GB}}(i,j) = \left[r_{ij}^2 + R_iR_j \exp\left(\frac{-r_{ij}^2}{4R_iR_j}\right)\right]^{1/2} \tag{17}$$

Here R_i are called the *effective Born radii.* The generalized Born approach is heavily used in biophysics because of its computational ease. However, generalized Born theory typically overestimates solvation free energies.

3 Nonlocal Born theory

An attempt to improve Born theory is “non-local Born theory”. Nonlocal Born theory takes into account nonlocality in the dielectric function of the solvent, which arrises because of correlations between solvent molecules. We start with equation 9 for the free energy change due to charging in a dielectric:

$$\begin{aligned} \Delta F &= \frac{\varepsilon\epsilon_0}{2}\int_V E^2 dV \\ &= \frac{1}{2}\int_V \boldsymbol{D}\cdot\boldsymbol{E} dV \\ &= \frac{1}{2\epsilon_0}\int_V \epsilon_0 D^2 - \boldsymbol{D}\cdot\boldsymbol{P} dV \end{aligned} \tag{18}$$

The first term is the free energy of charging in a vaccum, while the second term represents the additional free energy due to the dielectric. Therefore, the solvation free energy with respect to the vacuum is:

$$\Delta F_{\text{elec}} = \frac{1}{8\pi}\int_V 4\pi E^2 + \boldsymbol{P}\cdot\boldsymbol{E} dV \tag{19}$$

Now assume we have a nonlocal dielectric:

$$\boldsymbol{P}(\boldsymbol{r}) = \int d\boldsymbol{k} e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} \left(1 - \frac{1}{\varepsilon(k)}\right) \boldsymbol{D}(\boldsymbol{k}) \tag{20}$$

For a spherical ion of charge q and radius a one obtains:

$$\Delta F_{\text{elec}} = \frac{-q^2}{4\pi\epsilon_0} \int_0^\infty dk \frac{\sin^2 ka}{(ka)^2} \left(1 - \frac{1}{\varepsilon(k)}\right) \tag{21}$$

Literature results on nonlocal Born theory are mixed. It was shown that nonlocal Born theory performs worse than Born theory.[1] The reason for this is that nonlocal Born theory does not account for the rearrangement of solvent water molecules around the solute. The rearrangement of molecules in the first shell is extremely important. Other authors have shown that nonlocal Born theory can be made a bit more accurate than conventional Born theory by tuning the effective radii.

3.1 The effective potential & screening function

For a given $\varepsilon(k, 0)$ an effective potential can be derived such that :

$$\begin{aligned} \boldsymbol{E}(\boldsymbol{r}) &= -\nabla V_E(\boldsymbol{r}) \\ \boldsymbol{E}(\boldsymbol{k}) &= -i\boldsymbol{k} V_E(\boldsymbol{k}) \end{aligned} \tag{22}$$

We derive the expression by casting Gauss's law into Fourier space:

$$\begin{aligned} \nabla \cdot \boldsymbol{D}(\boldsymbol{r}) =& \rho(\boldsymbol{r}) \\ i\boldsymbol{k} \cdot \boldsymbol{D}(\boldsymbol{k}) =& \rho(\boldsymbol{k}) \\ i\boldsymbol{k} \cdot \epsilon_0 \varepsilon(\boldsymbol{k}) \boldsymbol{E}(\boldsymbol{k}) =& \rho(\boldsymbol{k}) \\ i\boldsymbol{k} \cdot \epsilon_0 \varepsilon(\boldsymbol{k})(-i\boldsymbol{k} V_E(\boldsymbol{k}) =& \rho(\boldsymbol{k}) \end{aligned} \tag{23}$$

$$V_E(\boldsymbol{k}) = \frac{\rho(\boldsymbol{k})}{\epsilon_0 \varepsilon(\boldsymbol{k}), 0) k^2} \tag{24}$$

Assuming isotropy one ends up with :

$$V_E(r) = \frac{1}{2\pi^2 \epsilon_0 r} \int_0^\infty \frac{\rho(k) \sin(kr)}{\varepsilon(k) k} \tag{25}$$

The screening factor is defined as:

$$S(r) = \frac{\varepsilon(0) 4\pi\varepsilon_0 r}{q} V_E \tag{26}$$

It is defined so that in a bulk medium S

$$V_E(\boldsymbol{r}) = \int \frac{d^3k}{(2\pi)^3} e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} \frac{\rho_{\text{f}}(\boldsymbol{k})}{\epsilon_0 \varepsilon(\boldsymbol{k}), 0) k^2} \tag{27}$$

4 Poisson-Boltzman equation

The Poisson-Boltzman (PB) equation was introduced by Gouy (1910) and Chapman (1913) and later elaborated by Debye and Hückel (1923). (When PB theory is applied to things like planar walls or cylinders, the term Gouy-Chapman theory is often used.) As it's name suggests, it is a combination of the Poisson equation for the electrostatic potential:

$$\nabla \cdot \varepsilon(\boldsymbol{r}) \nabla \phi(\boldsymbol{r}) = -\frac{1}{\epsilon_0} \rho(\boldsymbol{r}) \tag{28}$$

and the Boltzmann equation for the local density of ions. For each species s we have

$$n_s(\boldsymbol{r}) = \frac{N_s}{V} \exp\left(-\frac{q_s \phi(\boldsymbol{r})}{k_B T}\right) \tag{29}$$

We now assume we have an equal number of positive and negative ions (with the same valency) and substitute eqn. 29 into eqn. 28.

$$\begin{aligned}\nabla^2\phi &= \frac{qn_0}{\varepsilon\epsilon_0}\left[\exp\left(\frac{q\phi}{k_BT}\right) - \exp\left(-\frac{q\phi}{kT}\right)\right]\\ \nabla^2\phi &= \frac{qn_0}{\varepsilon\epsilon_0}\sinh\left(\frac{q\phi}{k_BT}\right)\end{aligned} \tag{30}$$

The linearized Poisson-Boltzman equation can be obtained by expanding the hyperbolic sine function in a Taylor series:

$$\begin{aligned}\nabla^2\phi(x) &= \Lambda^2\phi(x)\\ \Lambda^2 &\equiv \frac{2q^2n_0}{\varepsilon\epsilon_0 kT}\end{aligned} \tag{31}$$

Λ^{-1} is the Debye length. The solution of the linearized PB equation for the potential around a point charge is:

$$\phi(r) = A\frac{e^{-\Lambda r}}{r} \tag{32}$$

This screening function is the same as the Thomas-Fermi screening function for a free electron gas derived in Solid State physics textbooks from a different (but closely related) chain of logic. The longitudinal dielectric function can be related to the electrostatic potential via:

$$\phi(k) = -\frac{e}{q^2\epsilon\varepsilon_L(k)} = \frac{A}{1+k^2\Lambda^2} \tag{33}$$

This allows us to directly compute the nonlocal longitudinal susceptibility:

$$\chi_L(k) = \varepsilon_\infty - \frac{1}{\varepsilon_L(k)} = \frac{\varepsilon(0)-\varepsilon_\infty}{1+k^2\Lambda^2} + \varepsilon_\infty \tag{34}$$

This form has several nice properties:

$$\begin{aligned}\varepsilon(k) &\to \epsilon(0) \quad \text{as} \quad k \to 0\\ \varepsilon(k) &\to \epsilon_\infty \quad \text{as} \quad k \to \infty\\ \varepsilon(R) &\to \delta(R) \quad \text{as} \quad \lambda \to 0\end{aligned} \tag{35}$$

Somewhat confusingly, the same Lorentzian model can also be applied to $\varepsilon_L(k)$, assuming one makes the transformation $\lambda = \sqrt{\frac{\varepsilon_\infty}{\varepsilon(0)}}\Lambda$.[2] However, the Lorentzian formula fails dramatically for water (and most other molecular liquids) because it does not take into account large peaks in $\chi_L(k)$ due to overscreening, which is due the presence of local charge structure(s) and dipole-dipole correlations in the liquid. This points to the fact that the PBE neglects molecular structure and the presence of dipole-dipole correlations that exist in water's H-bond network. The presence of overscreening leads to an oscillatory structure in $\varepsilon(R)$, which indicates non-monotonic size dependence in the solvation energy of ions.[2] Such nontrivial dependence of solvation energy on ion size is found experimentally for water.

References

[1] T. Fonesca and B. Ladanyi. A molecular picture for eps(k) and its consequences for the energetics of ionic solvation. In M.P. Tossi and A.A. Kornyshev, editors, *Condensed Matter Physics Aspects of Electrochemistry.* World Scientific Press, Singapore, 1991.

[2] B. Mennucci and R. Cammi. *Continuum Solvation Models in Chemical Physics: From Theory to Applications.* Wiley, 2008.