Electrostatics Compendium
Electrostatic potentials in real space, reciprocal space and lattices

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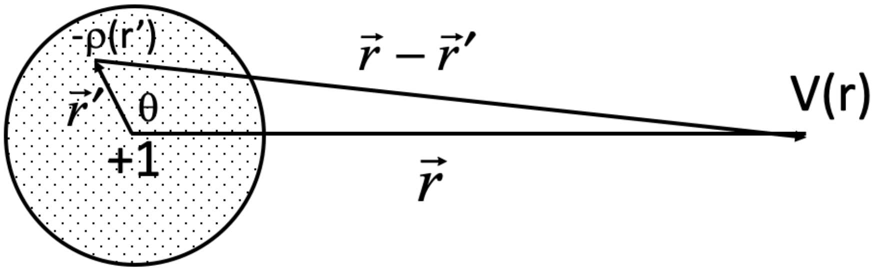

$$V(r) = \frac{e}{4\pi\varepsilon_0}\left[\frac{1}{r} - \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}'\right]$$

$$= \frac{e}{4\pi\varepsilon_0}\left[\left(\frac{1}{r} + \frac{1}{a}\right)e^{-2r/a}\right]$$

updated 10/16/21

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Introduction and Overview

These notes have been prepared (and revised, re-revised, etc.) over the past decades while working through various types of electrostatic problems encountered during our research. This interest in electrostatics grew out of three inter-related efforts:

1. My attempts to determine the "effective dielectric constant" of proteins from the shift in reduction potential upon modification of the net charge of a redox protein (J. Mol. Biol. 141, 323 (1980)).
2. Todd Yeates' numerical calculation of the electrostatic potential in the photosynthetic reaction center to evaluate the electrostatic contribution to the charge transfer asymmetry in this fascinating system (Yeates et al. PNAS 84, 6438 (1987)). This was at a time before the widespread availability of Poisson-Boltzmann equation solvers for proteins, which Todd skillfully developed for this purpose.
3. Barbara Hsu's efforts to experimentally evaluate the electrostatic potential around a protein by crystallographically determining the distribution of electron dense cations and anions (cesium and iodide, for example) in the solvent and relating this to the potential. This approach introduced me to the work of Bertaut and the value of the reciprocal space approach to solving electrostatic problems. The experimental accuracy required to reliably quantitate the electrostatic potential was not realistic at the time Barbara was conducting these studies, and unfortunately the project never progressed past the initial stages. With advances in x-ray diffraction data collection, and the possibility of using electron microscopy to get information on the electrostatic potential, this topic is worth re-visiting in my view.

As will become clear, these notes are not intended as a complete and systematic development of electrostatics, but rather reflect topics or problems I found of interest. This effort is a consequence of the "learn-by-doing" approach that I have found to be particularly useful when I am trying to learn new material.

NOTE: Since my proofreading and error correction skills are "imperfect", be aware that mistakes remain. If a derivation or equation doesn't make sense, don't exclude the possibility that it is because of errors in the text or equations.

Fundamental Relationships of Electrostatics

SI units
$q = 1.6022 \times 10^{-19}$ C
$4\pi\varepsilon_o = 1.1126 \times 10^{-10}$ C V^{-1} m^{-1}
$\varepsilon_0 = 8.8542 \times 10^{-12}$ C V^{-1} m^{-1}
1 J = 1 V x 1 C

cgs units
$e = 4.803 \times 10^{-10}$ esu (where esu^2 = erg cm)
1 statvolt = 10^{-8} c Volts = 299.792 Volts   ($c = 2.99792 \times 10^{10}$ cm sec^{-1})
1 erg = 10^{-7} J

$N_A = 6.0221 \times 10^{23}$ mol^{-1}
$k_B = R/N_A = 1.38066 \times 10^{-23}$ J K^{-1} = 1.38066×10^{-16} erg K^{-1}

electrostatic interaction energy and potential calculations are for unit (+1) charges separated by 10 Å = 10^{-9} m = 10^{-7} cm = 1 nm in ε = 1.

"chemical" units are in terms of valence charges (z = +1, -2, etc.) and distance r in Å.

Debye-Huckel parameters are calculated for aqueous solutions (ε = 78.5) at 298 K, with ionic strength, *I*, in moles/liter.

the ∇^2 operator for spherically symmetric systems is given by:

$$\nabla^2\Phi = \frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial\Phi}{\partial r} = \frac{1}{r}\frac{\partial^2(r\Phi)}{\partial r^2}$$

The Wikipedia section on cylindrical and spherical coordinates is very useful;
one neat relationship:

$$\nabla^2\Phi = \frac{1}{r}\frac{\partial^2(r\Phi)}{\partial r^2}$$

$$\text{if } \nabla^2\Phi = \kappa^2\Phi, \text{ then} \frac{\partial^2(r\Phi)}{\partial r^2} = \kappa^2(r\Phi) \Rightarrow r\Phi = Ae^{-\kappa r}$$

quantity	SI units	cgs units	“chemical” units
Poisson’s equation	$\nabla^2\Phi(r) = -\frac{\rho(r)}{\varepsilon_0\varepsilon}$	$\nabla^2\Phi(r) = -\frac{4\pi\rho(r)}{\varepsilon}$	
Coulomb energy	$\frac{q^2}{4\pi\varepsilon_o\varepsilon r}$	$\frac{e^2}{\varepsilon r}$	
numerical	$= \frac{(1.6022\times10^{-19})^2}{(1.1126\times10^{-10})(10^{-9})}$ $= 2.307\times10^{-19}$ J $\times N_A = 138.9$ kJ mol^{-1}	$= \frac{(4.8032\times10^{-10})^2}{(10^{-7})}$ $= 2.307\times10^{-12}$ erg $= 2.307\times10^{-19}$ J	$1389\frac{z_1z_2}{\varepsilon r}$ kJ/mole
electrostatic potential	$\frac{q}{4\pi\varepsilon_o\varepsilon r}$	$\frac{e}{\varepsilon r}$	
numerical	$= \frac{1.6022\times10^{-19}}{(1.1126\times10^{-10})(10^{-9})}$ $= 1.440$ V	$= \frac{4.8032\times10^{-10}}{10^{-7}}$ $= 0.00480$ statvolts $\times 299.79 = 1.440$ V	$14.40\frac{z}{\varepsilon r}$ V
Linearized PB equation	$\nabla^2\Phi(r) = \kappa^2\Phi(r) = -\frac{\rho(r)}{\varepsilon_0\varepsilon}$	$\nabla^2\Phi(r) = \kappa^2\Phi(r) = -\frac{4\pi\rho(r)}{\varepsilon}$	
$\Phi(r)$	$\frac{z_i q}{4\pi\varepsilon_0\varepsilon}\frac{e^{\kappa a}}{1+\kappa a}\frac{e^{-\kappa r}}{r}$	$\frac{z_i e}{\varepsilon}\frac{e^{\kappa a}}{1+\kappa a}\frac{e^{-\kappa r}}{r}$	
κ^2	$\frac{2000N_Aq^2}{\varepsilon\varepsilon_o k_BT}I$	$\frac{8\pi N_Ae^2}{1000\varepsilon k_BT}I$	
$1/\kappa$	$\sqrt{\frac{\varepsilon\varepsilon_o kT}{2000N_Aq^2}}\frac{1}{\sqrt{I}}$	$\sqrt{\frac{1000\varepsilon kT}{8\pi N_Ae^2}}\frac{1}{\sqrt{I}}$	
numerical	$\sqrt{\frac{(78.5)(8.85\times10^{-12})(1.38\times10^{-23})(298)}{2(6.02\times10^{23})(1000)(1.60\times10^{-19})^2}}\frac{1}{\sqrt{I}}$ $= \frac{3.041\times10^{-10}}{\sqrt{I}}$ m	$\sqrt{\frac{1000(78.5)(1.38\times10^{-16})(298)}{8\pi(6.02\times10^{23})(4.80\times10^{-10})^2}}$ $= \frac{3.041\times10^{-8}}{\sqrt{I}}$ cm	$= \frac{3.041}{\sqrt{I}}$ Å
$\ln\gamma_i$	$-\frac{z_i{}^2q^2}{8\pi\varepsilon_0\varepsilon k_BT}\kappa$	$-\frac{z_i{}^2e^2}{2\varepsilon k_BT}\kappa$	
$\ln\gamma_\pm$	$-\lvert z_+z_-\rvert\frac{q^2\kappa}{8\pi\varepsilon_0\varepsilon k_BT}$	$-\lvert z_+z_-\rvert\frac{e^2\kappa}{2\varepsilon k_BT}$	
$\log\gamma_\pm$			$-0.51\lvert z_+z_-\rvert\sqrt{I}$

Poisson's Equation

The electrostatic potential Φ = energy required to bring a single (+) charge q from $r = \infty$ (where $\Phi = 0$) to a point of potential Φ:

$$\Phi = \frac{q}{4\pi\varepsilon_0 \varepsilon r}$$

$$U = q_A \Phi$$

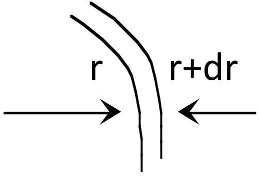
Notice that

$$\frac{d\Phi}{dr} = -\frac{q}{4\pi\varepsilon_0 \varepsilon r^2}$$

$$r^2 \frac{d\Phi}{dr} = -\frac{q}{4\pi\varepsilon_0 \varepsilon}$$

$$\Rightarrow \frac{d}{dr} r^2 \frac{d\Phi}{dr} = -\frac{dq/dr}{4\pi\varepsilon_0 \varepsilon}$$

For a time averaged, spherically symmetrical distribution of charge around a central ion in solution, the infinitesimal amount of charge, dq, in a shell of thickness dr is



with dq = ρ(r) x vol. of shell, where ρ (r) is the charge density

$$dq = \rho\left(4\pi r^2 dr\right)$$

$$\frac{dq}{dr} = 4\pi r^2 \rho$$

$$\text{since } \frac{d}{dr} r^2 \frac{d\Phi}{dr} = -\frac{dq/dr}{4\pi\varepsilon_0 \varepsilon} = -\frac{4\pi r^2 \rho}{4\pi\varepsilon_0 \varepsilon}$$

$$\text{therefore } \frac{d}{dr} r^2 \frac{d\Phi}{dr} \equiv r^2 \nabla^2 \Phi = -\frac{r^2 \rho}{\varepsilon_0 \varepsilon}$$

$$\Rightarrow \nabla^2 \Phi = -\frac{\rho}{\varepsilon_0 \varepsilon} \quad = \text{Poisson's equation}$$

where the ∇^2 operator (del squared or Laplacian) for spherically symmetric systems and cartesian coordinate systems may be written:

$$\nabla^2 \Phi = \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial \Phi}{\partial r} \left[= \frac{1}{r} \frac{\partial^2 (r\Phi)}{\partial r^2} \right] = \frac{\partial^2 \Phi}{\partial x^2} + \frac{\partial^2 \Phi}{\partial y^2} + \frac{\partial^2 \Phi}{\partial z^2} = -\frac{\rho(r)}{\varepsilon \varepsilon_0}$$

Poisson's equation relates charge density to the spatial variation of the potential gradient. This is a fundamental equation in electrostatics that we use in the analyses of the Debye-Huckel or Gouy-Chapman theories.

Electrostatics in Real and Reciprocal Space

May-June, 2008 (updated August 2008; October 2008; July 2010)
reformatted May 2021
more reformatting August 2021

reference: P. Coppens "X-ray Charge Densities and Chemical Bonding" Oxford University Press and the International Union of Crystallography (1997), esp. Chap. 8

notation

$\Phi(r) =$ real space potential = FT of $\psi(S)$

$\psi(S) =$ reciprocal space potential=FT of $\Phi(r)$

$\sigma(r) =$ spatial charge density

$\varphi(S) =$ FT of $\sigma(r)$

$F(S) =$ FT of real space charge distribution

relationship between $\Phi(r)$ and $\psi(h)$

Starting from Poisson's equation and following Coppens (Chapter 8)

$$\nabla^2\Phi(r) = -4\pi\rho_{\text{total}}(r) \quad (8.11)$$

$$\text{with } \nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

$$\nabla^2\Phi(r) = -\frac{\rho_{\text{total}}(r)}{\varepsilon\varepsilon_0} \quad \text{(SI units)}$$

where $\rho_{\text{total}}(r)$ is the electron density from both electrons and nuclei, so that

$$\Phi(r') = \sum_m \frac{z_m}{|r_m - r'|} - \int \frac{\rho(r)dr}{|r - r'|} \quad (8.3)$$

the Fourier transform of $\Phi(r)$, $\psi(h)$ (Coppens uses $\phi(H)$), may be derived

$$\Phi(r) = \int \psi(h)\exp[-2\pi i h \cdot r]dh \quad (8.12b)$$

$$\nabla^2\Phi(r) = -4\pi^2\int h^2\psi(h)\exp[-2\pi i h \cdot r]dh = -4\pi\rho_{\text{total}}(r) \quad (8.13)$$

$$\rho_{\text{total}}(r) = \int F_{\text{total}}(h)\exp[-2\pi i h \cdot r]dh$$

$$F_{\text{total}}(h) = \sum_A z_A \exp[+2\pi i h \cdot r_A] - F_{\text{electron}}(h) \quad \text{(sign in exponential changed 8/24/08)}$$

$$\psi(h) = \frac{F_{\text{total}}(h)}{\pi h^2} \quad (8.16) \quad (h^2 \text{ is actually the length}^2 \text{ of this vector } (=(ha^*)^2 \text{ Å}^{-2})$$

$$\psi(h) = \frac{F_{\text{total}}(h)}{4\pi^2\varepsilon_0 h^2} \quad \text{(SI)}$$

An excellent discussion of this topic is provided in the PhD thesis of Zhengwei Su, PhD thesis State University of Buffalo (1983), including treatment of the origin term.

Useful Fourier transformations and integrals

function	Fourier transform
$\frac{1}{r}$	$\frac{1}{\pi S^2} = \frac{1}{\pi h^2}$
$\frac{1}{\pi S^2}$	$\frac{1}{r}$
$\frac{\exp(-kr)}{r}$	$\frac{4\pi}{k^2 + 4\pi^2 S^2} = \frac{1}{\pi} \frac{1}{h^2 + \alpha^2}, k = 2\pi\alpha$

$$F(S) = \int_0^\infty \frac{2r}{S} f(r) \sin[2\pi Sr] dr$$

$$f(r) = \int_0^\infty \frac{2S}{r} F(S) \sin[2\pi Sr] dS$$

$$\frac{\pi}{2} = \int_0^\infty \frac{\sin[2\pi Sr]}{S} dS$$

$$\frac{4\pi}{k^2 + 4\pi^2 S^2} = 2\int_0^\infty e^{-kr} \frac{\sin[2\pi Sr]}{S} dr$$

Following Appendix 1 of Bertaut, the Fourier transform of 1/r may be derived as follows:

$$I = \int \frac{\exp[2\pi i \vec{h} \cdot \vec{r}]}{r} d\vec{r}$$

$$= \int \frac{\exp[2\pi i h r \cos\vartheta]}{r} r^2 \sin\vartheta dr d\vartheta d\varphi \quad \text{(taking } h \text{ as the polar axis)}$$

$$= 2\pi \int \exp[2\pi i h r \cos\vartheta] r \sin\vartheta d\vartheta dr$$

$$= 4\pi \int \frac{\sin[2\pi hr]}{2\pi hr} dr \text{ (note - Bertaut has "r" in denom.) [=} 4\pi \int \frac{\sin[2\pi hr]}{2\pi h} dr \quad \text{(Mathematica)]}$$

$$= \frac{1}{\pi h^2}$$

Bertaut gives the final result for this integral, but Mathematica states that the integral does not converge. Coppens has derived this result from Poisson's equation earlier in this section.

Also note that the Fourier transform of the screened Coulomb potential $\left(\frac{1}{\pi}\frac{1}{h^2+\alpha^2}\right)$ with $k = 2\pi\alpha = 0$ does give $\frac{1}{\pi h^2}$, but I'm not sure this limit is valid (Rob says it is!). The inverse Fourier transform of $\frac{1}{\pi h^2}$ gives $\frac{1}{r}$ as it should.

And, note that $1/h^2$ represents the distance squared in reciprocal space (ie $1/S^2$)

<u>Spherically averaged potential and Poisson's equation</u>

$F(S),\quad \psi(S)$ = Fourier transforms of radially symmetric charge distribution and potential

$$\begin{aligned}\Phi(r) &= \int_0^\infty \frac{2S}{r}\psi(S)\sin(2\pi Sr)\,dS \\ &= \int_0^\infty \frac{2S}{r}\frac{F(S)}{\pi S^2}\sin(2\pi Sr)\,dS \\ &= \int_0^\infty \frac{2F(S)}{\pi S}\frac{\sin(2\pi Sr)}{r}\,dS\end{aligned}$$

when F is in electrons, S in $Å^{-1}$ and r in Å, the overall units for the potential are e/Å. Multiplying this by 1369 gives the energy in kJ /mole, and dividing by 96.5 =14.4 gives the result in Volts.

<u>Poisson's equation (spherical coordinates)</u>

$$-\frac{1}{4\pi}\nabla^2\Phi(r) = \rho(r)$$

$$\text{with } \nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}$$

$$-\frac{1}{4\pi}\nabla^2\Phi(r) = -\frac{1}{4\pi}\int_0^\infty \frac{2F(S)}{\pi S}\nabla^2\frac{\sin(2\pi Sr)}{r}\,dS$$

$$\nabla^2\frac{\sin(2\pi Sr)}{r} = -\frac{4\pi^2 S^2}{r}\sin(2\pi Sr)$$

$$\begin{aligned}-\frac{1}{4\pi}\nabla^2\Phi(r) &= -\frac{1}{4\pi}\int_0^\infty \frac{2F(S)}{\pi S}\left(-\frac{4\pi^2 S^2}{r}\sin(2\pi Sr)\right)dS \\ &= \int_0^\infty \frac{2S}{r}F(S)\sin(2\pi Sr)\,dS = \rho(r)\end{aligned}$$

Poisson’s equation (Cartesian, orthogonal)

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

$$-\frac{1}{4\pi}\nabla^2\Phi(r) = -\frac{1}{4\pi V}\nabla^2\sum_{hkl}\frac{1}{\pi\left(\left(ha^*\right)^2+\left(kb^*\right)^2+\left(lc^*\right)^2\right)}F(hkl)\cos\left(2\pi\left(ha^*x+kb^*y+lc^*z\right)\right)$$

$$= -\frac{-4\pi^2}{4\pi^2 V}\sum_{hkl}\frac{\left(\left(ha^*\right)^2+\left(kb^*\right)^2+\left(lc^*\right)^2\right)}{\left(\left(ha^*\right)^2+\left(kb^*\right)^2+\left(lc^*\right)^2\right)}F(hkl)\cos\left(2\pi\left(ha^*x+kb^*y+lc^*z\right)\right)$$

$$\rho = \frac{1}{V}\sum_{hkl}F(hkl)\cos\left(2\pi\left(ha^*x+kb^*y+lc^*z\right)\right)$$

the units of Φ when F is in e, V is in $Å^3$ and S is in $Å^{-1}$ is again e/Å.

Real and Reciprocal Space Electrostatics – Test Calculations

Self-charging of spherical ions

"Classical analysis" (?) of incrementally building up an ion of overall radius R, uniform charge density ρ and total charge Q

$$W_S = \int_0^Q \frac{q(r)\,dq(r)}{r}$$

$$\rho = \frac{Q}{(4\pi/3)R^3}$$

$$q(r) = \frac{(4\pi/3)r^3}{(4\pi/3)R^3}Q = \frac{r^3}{R^3}Q; \quad r = R\left(\frac{q}{Q}\right)^{1/3}$$

$$dq(r) = \frac{3r^2}{R^3}Q\,dr$$

$$W_S = \int_0^Q \frac{q(r)\,dq(r)}{r} = \frac{Q^{1/3}}{R}\int_0^Q \frac{q\,dq}{q^{1/3}} = \frac{3Q^2}{5R}$$

$$= \int_0^Q \frac{q(r)\,dq(r)}{r} = \frac{3Q^2}{R^6}\int_0^R \frac{r^3 \cdot r^2}{r}\,dr = \frac{3Q^2}{R^6}\int_0^R r^4\,dr = \frac{3Q^2}{5R}$$

(in the Born self charging energy, the radius is fixed at R, and charge dq is incrementally added to the surface of the sphere from r = ∞)

Following Bertaut's analysis (Eq. 33), $W_S' = \sum_i q_i^2 \int_{-\infty}^{\infty} \left|\varphi(h)\right|^2 dh$

For a uniform spherical charge of radius R, $\sigma(r) = \frac{3}{4\pi R^3}, \quad r \le R$ (Eqs. 36-37)

$$\varphi(h) = \frac{3}{4\pi R^3}\frac{2}{h}\int_0^R r\sin\left[2\pi h r\right]dr$$

$$= 3\frac{\sin\alpha - \alpha\cos\alpha}{\alpha^3} \quad \text{with } \alpha = 2\pi h R \quad \text{(Eq. 40)}$$

$$\int_{-\infty}^{\infty} \left|\varphi(h)\right|^2 dh = \frac{9}{2\pi R}\int_{-\infty}^{\infty}\left(\frac{\sin\alpha - \alpha\cos\alpha}{\alpha^3}\right)^2 d\alpha$$
$$= \frac{3}{5R}$$
$$\text{and } W_S' = \frac{3}{5R}\sum_i q_i^2$$

(why isn't $\int_{-\infty}^{\infty}\left|\varphi(h)\right|^2 dh$ with the volume integral $4\pi h^2 dh$?? This must be related to eq 1.2 of Bertaut's 1978 paper that writes the self energy as $\frac{1}{2\pi}\int_0^\infty \frac{\left|\varphi(\vec{h})\right|^2}{\left|\vec{h}\right|^2} d^3\vec{h}\sum_j q_j^2$)

Potential of a spherical (Gaussian) charge at the origin

$$\sigma(r) = \left(\frac{a}{\pi}\right)^{3/2}\exp\left[-ar^2\right] \quad \text{(corrected 8/19/08 from } \left(\frac{a}{r}\right)^{3/2}\text{)}$$
$$\varphi(S) = \exp\left[-\pi^2 S^2/a\right] \equiv \exp\left[-bS^2\right] \quad \text{(corrected 8/19/08 from } \exp\left[-\pi^2 S^2/a^2\right]\text{)}$$

The Fourier transform of the potential is (see charge1.nb)

$$\Phi(r) = \int_0^\infty \frac{2S}{r}\frac{\varphi(S)}{\pi S^2}\sin\left[2\pi S r\right]dS = \frac{2}{\pi r}\int_0^\infty \frac{\exp\left[-bS^2\right]}{S}\sin\left[2\pi S r\right]dS$$
$$= \frac{2}{\pi r}\frac{\pi}{2}\text{Erf}\left[\frac{\pi r}{\sqrt{b}}\right]$$

From Abramowitz & Stegun (pg 298), the asymptotic form of Erf is

$$\text{Erfc}\left[z\right] = \frac{1}{\sqrt{\pi}z}\exp\left[-z^2\right] = 1 - \text{Erf}\left[z\right]$$
$$\text{Erf}\left[z\right] = 1 - \frac{\exp\left[-z^2\right]}{\sqrt{\pi}z}$$

Giving

$$\Phi(r) = \frac{2}{\pi r}\frac{\pi}{2}\text{Erf}\left[\frac{\pi r}{\sqrt{b}}\right] = \frac{1}{r}\text{Erf}\left[\frac{\pi r}{\sqrt{b}}\right]$$
$$= \frac{1}{r}\left(1 - \frac{\exp\left[-\pi^2 r^2/b\right]}{\pi r}\sqrt{\frac{b}{\pi}}\right) \approx \frac{1}{r}$$

(8/19/08: Wikipedia (http://en.wikipedia.org/wiki/Electrical_potential) gives the corresponding result for the electrical potential of a “tridimensional spherically symmetric Gaussian charge density” calculated using Poisson’s equation:

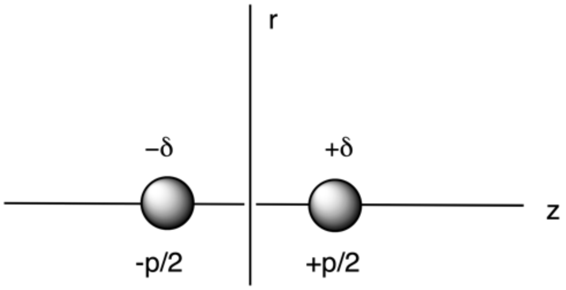
$$\rho(r)=\frac{q}{\sqrt{2\pi\sigma^2}}e^{-r^2/2\sigma^2};\nabla^2\Phi=-4\pi\rho;\Phi(r)=\frac{q}{r}Erf\left[\frac{r}{\sqrt{2\sigma^2}}\right])$$

Uniform spherical charge of radius R

$$\varphi(S)=3\frac{\sin[2\pi SR]-2\pi SR\cos[2\pi SR]}{(2\pi SR)^3}$$

$$\begin{aligned}\Phi(r)&=\frac{6}{\pi r}\int_0^\infty\frac{1}{S}\left(\frac{\sin[2\pi SR]-2\pi SR\cos[2\pi SR]}{(2\pi SR)^3}\right)\sin[2\pi SR]dS\\&=\frac{1}{4rR^3}\left[abs(r-R)^3-(r+R)^3+3R\left((r-R)^2 sign(r-R)+(r+R)^2\right)\right]\\&=\frac{1}{r},\quad r>R\\&=\frac{1}{2R}\left(3-\frac{r^2}{R^2}\right),\quad r<R\end{aligned}$$

Dipole of point charges (±δ) at z = ±(p/2)



The Fourier transform of this charge distribution is:

$$F(\vec{S})=\frac{\delta}{\pi S^2}\varphi(\vec{S})\left(\exp[i\pi\vec{p}\cdot\vec{S}]-\exp[-i\pi\vec{p}\cdot\vec{S}]\right)$$

in cylindrical coordinates $S^2=t^2+\zeta^2;\quad S\cos\vartheta=\zeta;\quad S\sin\vartheta=t$, so

$$F(\vec{S})=F(t,\zeta)=\frac{2i\delta\varphi(t,\zeta)}{\pi(t^2+\zeta^2)}\sin[\pi p\zeta]$$

The significance of the imaginary value for $F(t,\zeta)$ will be discussed below.

For point charges where $\varphi(\vec{S})=1$, the Fourier-Bessel transform gives for the potential

$$\Phi(R,Z)=\int_{-\infty}^{\infty}\left\{\int_{0}^{\infty}2\pi t F(t,\zeta)J_0(2\pi Rt)\,dt\right\}\exp\left[-2\pi i\zeta Z\right]d\zeta$$

$$=4i\delta\int_{-\infty}^{\infty}\left\{\int_{0}^{\infty}\frac{t}{t^2+\zeta^2}J_0(2\pi Rt)\,dt\right\}\sin\left[\pi p\zeta\right]\exp\left[-2\pi i\zeta Z\right]d\zeta$$

$$=8\delta\int_{0}^{\infty}tJ_0(2\pi Rt)\left\{\int_{0}^{\infty}\frac{\sin\left[\pi p\zeta\right]\sin\left[2\pi Z\zeta\right]}{t^2+\zeta^2}d\zeta\right\}dt$$

The integral in brackets may be evaluated from 3.742.1 (page 415) of Gradshteyn and Ryzhik:

$$\int\frac{\sin ax\sin bx}{\beta^2+x^2}dx=\frac{\pi}{4\beta}\left(\exp\left[-(a-b)\beta\right]-\exp\left[-(a+b)\beta\right]\right)\quad a>b>0,\mathrm{Re}\,\beta>0$$

$$b=\pi p,\quad a=2\pi Z,\quad x=\zeta,\quad \beta=t$$

$$\int_{0}^{\infty}\frac{\sin\left[\pi p\zeta\right]\sin\left[2\pi Z\zeta\right]}{t^2+\zeta^2}d\zeta=\frac{\pi}{4t}\left(\exp\left[-(2\pi Z-\pi p)t\right]-\exp\left[-(2\pi Z+\pi p)t\right]\right)$$

with the result

$$\Phi(R,Z)=8\delta\int_{0}^{\infty}tJ_0(2\pi Rt)\left\{\int_{0}^{\infty}\frac{\sin\left[\pi p\zeta\right]\sin\left[2\pi Z\zeta\right]}{t^2+\zeta^2}d\zeta\right\}dt$$

$$=2\pi\delta\int_{0}^{\infty}\left[J_0(2\pi Rt)\left(\exp\left[-(2\pi Z-\pi p)t\right]-\exp\left[-(2\pi Z+\pi p)t\right]\right)\right]dt$$

using the integral (from Mathematica, also 6.621.1 (page 711 of G&R with F(0, ; ;) = 1)

$$\int_{0}^{\infty}\exp\left[-at\right]J_0(bt)\,dt=\frac{1}{\sqrt{a^2+b^2}}=\frac{1}{a\sqrt{1+b^2/a^2}}$$

this expression may be reduced to

$$2\pi\delta\left[\frac{1}{2\pi Z-\pi p}\frac{1}{\sqrt{1+\left((2\pi R)^2/(2\pi Z-\pi p)^2\right)}}-\frac{1}{2\pi Z+\pi p}\frac{1}{\sqrt{1+\left((2\pi R)^2/(2\pi Z+\pi p)^2\right)}}\right]$$

with $Z >> p$, this expression may be expanded in powers of *(p/2Z)* (Mathematica dipole_calcs.nb)

$$\Phi(R,Z)=\left[\frac{2\delta}{Z\sqrt{1+\left(R^2/Z^2\right)}}-\frac{2\delta R^2}{\left(Z\sqrt{1+\left(R^2/Z^2\right)}\right)^3}\right]\left(\frac{p}{2Z}\right)+O\left(\left(\frac{p}{2Z}\right)^3\right)$$

with $\frac{1}{\sqrt{1+\left(R^2/Z^2\right)}}=\frac{1}{\sqrt{1+\left(\sin^2\vartheta/\cos^2\vartheta\right)}}=\cos\vartheta$

$$=\frac{p\delta\cos\vartheta}{Z^2}-\frac{p\delta R^2\cos^3\vartheta}{Z^4}$$

this may be rearranged to give the distance dependence in terms of the distance r, where $r^2=Z^2+R^2$ and $Z=r\cos\vartheta$

$$=\frac{p\delta\cos\vartheta}{Z^2}\left[1-\frac{R^2\cos^2\vartheta}{Z^2}\right]=\frac{p\delta\cos\vartheta}{Z^2}\left[1-\tan^2\vartheta\cos^2\vartheta\right]$$

$$=\frac{p\delta\cos\vartheta}{Z^2}\left[1-\sin^2\vartheta\right]=\frac{p\delta\cos\vartheta}{1}\frac{\left[\cos^2\vartheta\right]}{Z^2}$$

$$=\frac{p\delta\cos\vartheta}{r^2}$$

Which is the correct expression!!! The dipole moment $\mu=p\delta$.

Dipole potential of Gaussian charges

$$\Phi(R,Z)=\int_{-\infty}^{\infty}\left\{\int_{0}^{\infty}2\pi tF(t,\zeta)J_0(2\pi tR)\,dt\right\}\exp\left[-2\pi i\zeta Z\right]d\zeta$$

$$F(t,\zeta)=\frac{2i\delta\varphi(t,\zeta)}{\pi\left(t^2+\zeta^2\right)}\sin\left[\pi p\zeta\right]$$

for a Gaussian, $\varphi(t,\zeta)=\exp\left[-bS^2\right]=\exp\left[-bt^2\right]\exp\left[-b\zeta^2\right]$

$$\Phi(0,Z)=4i\delta\int_{-\infty}^{\infty}\left\{\int_{0}^{\infty}\frac{t\exp\left[-bt^2\right]}{\left(t^2+\zeta^2\right)}dt\right\}\exp\left[-b\zeta^2\right]\sin\left[\pi p\zeta\right]\exp\left[-2\pi i\zeta Z\right]d\zeta$$

$$\int_{0}^{\infty}\frac{t\exp\left[-bt^2\right]}{\left(t^2+\zeta^2\right)}dt=\frac{1}{2}\exp\left[b\zeta^2\right]\Gamma\left(0,b\zeta^2\right)$$

$$\begin{aligned}\Phi(0,Z)&=2i\delta\int_{-\infty}^{\infty}\Gamma\left(0,b\zeta^2\right)\sin\left[\pi p\zeta\right]\exp\left[-2\pi i\zeta Z\right]d\zeta\\&=2i\delta\int_{0}^{\infty}\Gamma\left(0,b\zeta^2\right)\sin\left[\pi p\zeta\right]\left(\exp\left[-2\pi i\zeta Z\right]-\exp\left[2\pi i\zeta Z\right]\right)d\zeta\\&=4\delta\int_{0}^{\infty}\Gamma\left(0,b\zeta^2\right)\sin\left[\pi p\zeta\right]\sin\left[2\pi\zeta Z\right]d\zeta\end{aligned}$$

I couldn’t derive an asymptotic expression for this, for large Z, or Z >> p, but when numerically integrated with Mathematica in dipole3.nb, this gives correct values of $\Phi(0,Z)=p\delta/Z^2$ with b=10, p=1, and Z varying between 5 to 50.

Significance of imaginary scattering factor for the dipole potential

When $F\left(h\right)=\left|F\left(h\right)\right|\exp\left[\pm i\frac{\pi}{2}\right],\quad \rho\left(r\right)=-\rho\left(-r\right)$, which is the symmetry of the dipole potential.

Proof:

$$\rho\left(r\right)=\frac{1}{V}\sum_{all:h}\left|F\left(h\right)\right|\left(\exp\left[i\alpha\right]\exp\left[-2\pi ih\cdot r\right]\right)$$

$$\rho\left(r\right)=\frac{1}{V}\sum_{h\geq 0}\left|F\left(h\right)\right|\left(\exp\left[i\frac{\pi}{2}\right]\exp\left[-2\pi ih\cdot r\right]+\exp\left[-i\frac{\pi}{2}\right]\exp\left[2\pi ih\cdot r\right]\right)$$

$$=\frac{2}{V}\sum_{h\geq 0}\left|F\left(h\right)\right|\left(\cos\left[2\pi ih\cdot r-\frac{\pi}{2}\right]\right)=\frac{2}{V}\sum_{h\geq 0}\left|F\left(h\right)\right|\left(\sin\left[2\pi ih\cdot r\right]\right)$$

$$\rho\left(-r\right)=-\frac{2}{V}\sum_{h\geq 0}\left|F\left(h\right)\right|\left(\sin\left[2\pi ih\cdot r\right]\right)=-\rho\left(r\right)$$

Hydrogen atom electrostatics test calculations

$$\rho(r) = \frac{1}{\pi a^3} e^{-2r/a}$$

$$F(S) = \frac{1}{\left(1+(\pi S a)^2\right)^2}$$

$$\rho(r) = \int_0^\infty \frac{2S}{r} F(S) \sin(2\pi S r)\, dS$$

$$F(S) = \int_0^\infty \frac{2r}{S} \rho(r) \sin(2\pi S r)\, dr$$

Fourier transforms of electrostatic potentials from proton and electron:

$$\psi_+(S) = \frac{1}{\pi S^2}$$

$$\psi_-(S) = \frac{1}{\pi S^2} \frac{1}{\left(1+(\pi S a)^2\right)^2}$$

$$\begin{aligned} \psi_{tot}(S) &= \psi_+(S) - \psi_-(S) \\ &= \pi a^2 \frac{2+(\pi S a)^2}{\left(1+(\pi S a)^2\right)^2} \end{aligned}$$

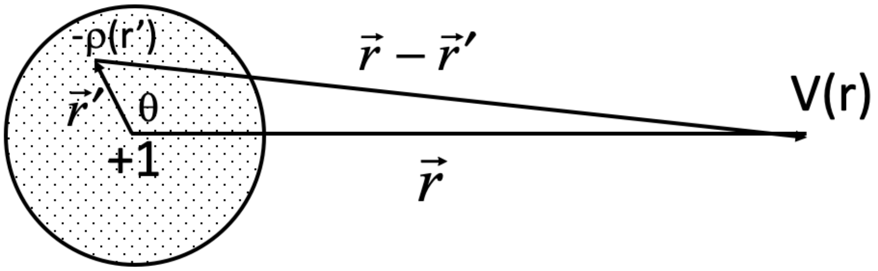
electrostatic potential around a hydrogen atom (see Hatom_electrostatics.nb)

$$\begin{aligned} \Phi(r) &= \int_0^\infty \frac{2S}{r} \psi(S) \sin(2\pi S r)\, dS \\ &= \pi a^2 \int_0^\infty \frac{2S}{r} \frac{2+(\pi S a)^2}{\left(1+(\pi S a)^2\right)^2} \sin(2\pi S r)\, dS \\ &= \left(\frac{1}{r} + \frac{1}{a}\right) e^{-2r/a} \end{aligned}$$

this equation satisfies Poisson’s equation (equal to –electron density of electron) (must also contain a term δ(0) for the proton, but this didn’t come out explicitly)

Direct calculation of the Coulomb's law electrostatic potential for the hydrogen atom

Define the following coordinate system for hydrogen with the origin at the proton:



The electrostatic potential, V(r), at the point r may be expressed

$$V(r)=\frac{e}{4\pi\varepsilon_0}\left[\frac{1}{r}-\int\frac{\rho(\vec{r}')}{|\vec{r}-\vec{r}'|}d\vec{r}'\right]$$

Eq. 15

$$=\frac{e}{4\pi\varepsilon_0}\left[\frac{1}{r}-\int_0^\infty r'^2\,dr'\int_0^\pi \sin\vartheta\,d\vartheta\int_0^{2\pi}d\varphi\left[\frac{\rho(\vec{r}')}{\left(r^2+r'^2-2rr'\cos\vartheta\right)^{1/2}}\right]\right]$$

with $\rho(r)=\frac{1}{\pi a^3}e^{-2r/a}$, this expression may be integrated (I did this with Mathematica – H_atom_electron_scattering_factors_calculations_Sept2021.nb) to give

Eq. 16

$$V(r)=\frac{e}{4\pi\varepsilon_0}\left[\left(\frac{1}{r}+\frac{1}{a}\right)e^{-2r/a}\right]$$

Note that even though the hydrogen atom is electrically neutral, the potential V(r) is always positive!

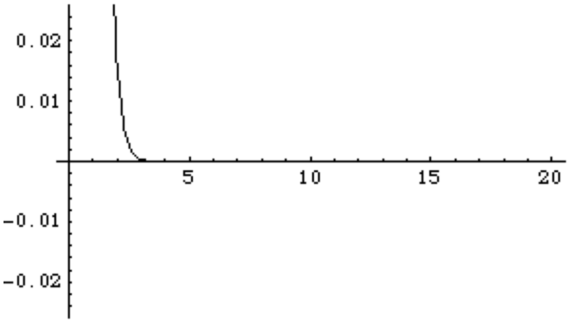
numerical values
with charges in units of proton charge and distances in Å (a = 0.529 Å)

$$\Phi(r)=\left(\frac{1}{r}+\frac{1}{a}\right)e^{-2r/a}$$

$$=1389\left(\frac{1}{r}+\frac{1}{a}\right)e^{-2r/a}\text{ kJ/mole}$$

$$=\frac{1389}{96.5}\left(\frac{1}{r}+\frac{1}{a}\right)e^{-2r/a}\text{ V}$$

```
fact = 1389 / 96.5
b = 0.529
pottot[r_] := fact * ((1 / r) + (1 / b)) * Exp[-2 r / b]
Plot[{potplus[r], potneg[r], pottot[r]}, {r, 0.1, 20.}, PlotRange → {-.026, .026},
 AxesOrigin -> {0, 0}]
```



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(from Hatom_electrostatics.nb)

note: $\Phi(r) \sim 0.026V$ for $r \sim 1.9\mathring{A}$ (kT ~ 0.026V at RT)

units

e_0 = 8.85419 x 10^{-12} $C^2/(Nm)^2$ (/) = 4.8032 x 10^{-10} esu ($cm^{3/2}$ $gm^{½}$ s^{-1})

q = 1.60218 x 10^{-19} Coulomb (1 C = 6.241 x 10^{18} charges)

N = 6.02221 x 10^{23} mol^{-1}

F = 96.485 kJ/V

$$\frac{e^2 \quad (\text{charge})}{r \quad (\text{Å})} = \frac{\left(1.6022\times10^{-19}\right)^2}{4\pi\left(\varepsilon_0 = 8.854\times10^{-12}\right)10^{-10}} \times 6.0221\times10^{23}$$

$$= 1389.4 \text{ kJ/mole}$$

$$= 14.40 \text{ V}$$

Coppens eq (8.24) for $\psi(0)$, with $\rho_{tot}(r) = \frac{1}{\pi a^3} e^{-2r/a}$ (δ(0) for the proton omitted since r^2=0 at the origin).

$$\psi(0) = \frac{2\pi}{3V} \int_{cell} r^2 \rho_{tot}(\vec{r})\, d\vec{r}$$

$$= \frac{2\pi}{3} \int_0^\infty r^2 \rho_{tot}(r)\, 4\pi r^2\, dr$$

$$= \frac{8\pi}{3a^3} \int_0^\infty r^4 e^{-2r/a}\, dr$$

with $\int_0^\infty x^n e^{-\alpha x}\, dx = \frac{n!}{\alpha^{n+1}}$ and n=4, $\alpha = 2/a$

$$\psi(0) = 2\pi a^2$$

which is the value calculated directly from the expression:

$$\psi_{tot}(S) = \pi a^2 \frac{2 + (\pi S a)^2}{\left(1 + (\pi S a)^2\right)^2}$$

Bertaut's lattice sum evaluation of electrostatic energies

F. Bertaut, L'énergie électrostatique de réseaux ioniques. *J. Phys. Radium* **13**, 499-505 (1952)
E.F. Bertaut, Electrostatic potentials, fields and field gradients. *J. Phys. Chem. Solids* **39**, 97-102 (1978)

Bertaut writes the total electrostatic energy, W_T, as the sum of two terms: W_i, that gives the energy due to interacting charges, and W_S, the self energy, which is infinite for point charges.

$$W_T = W_i + W_S$$

$$W_T = \frac{1}{2}\sum_i \sum_j \frac{q_i q_j}{r_{ij}} = \frac{1}{2}\sum_{i\neq j} \frac{q_i q_j}{r_{ij}} + W_S$$

$$= \frac{1}{2\pi V}\sum_h \frac{\left|F(h)\right|^2}{h^2} \quad \text{(Eq. 15)}$$

This relationship reflects that the Patterson function at a position r is the sum of the products of the electron density separated by a distance r.

Bertaut realized that a finite value for W_T would be obtained if self energy was evaluated, not for point charges, but for non-overlapping spatial charge densities, $\sigma(r)$

$$W_T{}' = \frac{1}{2\pi V}\sum_h \frac{\left|F(h)\right|^2 \left|\varphi(h)\right|^2}{h^2} \quad \text{(Eq. 24)}$$

$$\text{with } \varphi(h) = \int \sigma(r)\exp\left[2\pi i h r\right] dr = \int_0^R 4\pi r^2 \sigma(r)\frac{\sin 2\pi h r}{2\pi h r}\, dr = \int_0^R \frac{2r}{h}\sigma(r)\sin 2\pi h r\, dr$$

where the latter relations are valid for a spherically symmetric object.

the self energy is given by

$$W_S{}' = \frac{1}{2}\sum_i q_i^2 \int \frac{P(\vec{u})}{u} d\vec{u} \quad \text{(Eq. 28)}$$

$$= \sum_i q_i^2 \int_{-\infty}^{\infty} \left|\varphi(h)\right|^2 dh \quad \text{(Eq. 33)}$$

$$\text{for a uniform sphere, } \sigma(r) = \frac{3}{4\pi R^3}, \quad r \leq R \quad \text{(Eqs. 36-37)}$$

$$\varphi(h) = 3\frac{\sin\alpha - \alpha\cos\alpha}{\alpha^3} \quad \text{with } \alpha = 2\pi h R \quad \text{(Eq. 40)}$$

$$W_S{}' = \frac{3}{5R}\sum_i q_i^2 \quad \text{(for a uniform sphere; Eq. 39)}$$

The interaction energy between ionic residues in a lattice may be calculated from Eq. 41

$$W_i = W_T' - W_S'$$

$$W_i = \frac{18\pi R^2}{V}\sum_h \left|F(h)\right|^2 \frac{\left(\sin\alpha - \alpha\cos\alpha\right)^2}{\alpha^8} - \frac{3}{5R}\sum_j q_j^2$$

with $F(h) = \sum_k q_k \exp\left[2\pi i h\cdot x_k\right]$ (Eq. 6) and $\alpha=2\pi hR$

Following (loosely) Templeton (*J. Chem. Phys.* **23**, 1629 (1955)), W_i may related to the Madelung constant, A (or M in Bertaut) through the expression

$$A = -\frac{W_i L}{e^2 Z}$$

where W_i is the interaction energy per unit cell; L is the distance between closest, oppositely charged ions (defined in terms of the cell axis length) and Z is the number of molecules per unit cell.

Following Bertaut, expressions for W_i may be derived as follows:

fcc structure (NaCl, a = 5.63 Å; KCl, a = 6.29 Å)

$$R = \frac{a}{4} \text{ (the minimum ion-ion distance = } \frac{a}{2}\text{)}$$

$$W_i = \frac{e^2}{a}\left[72\pi \sum_{h,k,l \text{ odd}} \frac{g^2}{\alpha^4}\right] - \frac{3}{5}\frac{4}{a}\left[8e^2\right] = \frac{e^2}{a}\left[72\pi \sum_{h,k,l \text{ odd}} \frac{g^2}{\alpha^4} - 19.2\right]$$

$$\alpha = 2\pi\frac{\sqrt{h^2+k^2+l^2}}{a}\frac{a}{4} = \frac{\pi}{2}\sqrt{h^2+k^2+l^2}$$

$$g = \frac{\left(\sin\alpha - \alpha\cos\alpha\right)}{\alpha^2}$$

$$A = -\frac{W_i L}{e^2 Z} = -\frac{W_i}{e^2}\frac{a}{2}\frac{1}{4} \sim 1.747558 \text{ (Kittel)}$$

bcc structure (CsCl, a = 4.11 Å)

$$R = \frac{\sqrt{3}}{4}a \text{ (the minimum ion-ion distance = } \frac{\sqrt{3}}{2}a\text{)}$$

$$F\left(h\right) = e\left[1 - \exp\left[\pi i\left(h + k + l\right)\right]\right] = 2e \ (h{+}k{+}l \ odd), \ 0 \ (h{+}k{+}l \ even)$$

$$W_i = \frac{e^2}{a}\left[13.5\pi \sum_{h+k+l \text{ odd}} \frac{g^2}{\alpha^4}\right] - \frac{3}{5}\frac{4}{\sqrt{3}a}\left[2e^2\right] = \frac{e^2}{a}\left[13.5\pi \sum_{h+k+l \text{ odd}} \frac{g^2}{\alpha^4} - \frac{24}{5\sqrt{3}}\right]$$

$$\alpha = 2\pi \frac{\sqrt{h^2 + k^2 + l^2}}{a}\frac{\sqrt{3}a}{4} = \frac{\sqrt{3}\pi}{2}\sqrt{h^2 + k^2 + l^2}$$

$$g = \frac{\left(\sin\alpha - \alpha\cos\alpha\right)}{\alpha^2}$$

$$A = -\frac{W_i L}{e^2 Z} = -\frac{W_i}{e^2}\frac{\sqrt{3}a}{2}\frac{1}{1} \sim 1.762670 \text{ (Kittel)}$$

A simple Fortran program (Bertaut.f) summing up to maximum indices of 50 gives values of the Madelung constants of 1.747606 and 1.762705 (accurate to < 0.003%; after hmax = 5, the values are accurate to < 0.1% and 0.02%, respectively.

Jones and Templeton (*J. Chem. Phys.* **25**, 1062 (1956) have derived different expressions for the shape function that give improved convergence.

Electrostatic calculations in a planar and membrane systems

Electrostatic potential in a planar (slab) system (test calculations for membranes)

consider a system with two infinite and oppositely charged planes perpendicular to the z axis and crossing at +p and –p. For now, consider that the charge is everywhere zero, except it equals +1 at z = +p and -1 at z = -p.

$$F(S) = e^{2\pi iSp} - e^{-2\pi iSp}$$

$$\psi(S) = \frac{e^{2\pi iSp} - e^{-2\pi iSp}}{\pi S^2} = \frac{2i\sin(2\pi Sp)}{\pi S^2}$$

$$\Phi(Z) = \frac{2i}{\pi}\int_{-\infty}^{\infty} \frac{\sin(2\pi Sp)}{S^2} e^{-2\pi iSZ}\, dS$$

$$= \frac{2i}{\pi}\int_{-\infty}^{\infty} \frac{\sin(2\pi Sp)\cos(2\pi SZ)}{S^2} dS + \frac{2}{\pi}\int_{-\infty}^{\infty} \frac{\sin(2\pi Sp)\sin(2\pi SZ)}{S^2} dS$$

$$\frac{2i}{\pi}\int_{-\infty}^{\infty} \frac{\sin(2\pi Sp)\cos(2\pi SZ)}{S^2} dS = 0$$

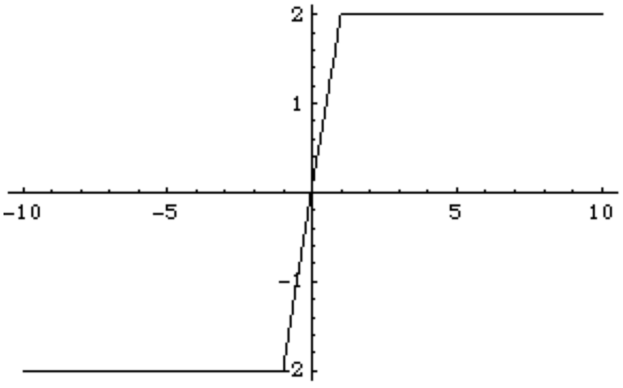
$$\frac{2}{\pi}\int_{-\infty}^{\infty} \frac{\sin(2\pi Sp)\sin(2\pi SZ)}{S^2} dS = 2\pi\left(-|p-Z| + |p+Z|\right)$$

$$\therefore \Phi(Z) = 2\pi\left(-|p-Z| + |p+Z|\right)$$

between the plates (-p < Z < p), $\Phi(Z) = 4\pi Z$

(capacitor.nb)

```
Plot[-Abs[1 - z] + Abs[1 + z], {z, -10, 10}]
```



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the voltage drop is linear between the charged surfaces (constant electric field). Outside the surfaces, the potential has values ± 4πp, so the total voltage drop is equal to 8πp or 4πd, where d = the separation distance.

Same calculation as above, but using SI units (ie, divide through by $4\pi\varepsilon_0$))

$$F(S) = e^{2\pi iSp} - e^{-2\pi iSp}$$

$$\psi(S) = \sigma \frac{e^{2\pi iSp} - e^{-2\pi iSp}}{4\pi^2 \varepsilon_0 S^2} = \sigma \frac{2i\sin(2\pi Sp)}{4\pi^2 \varepsilon_0 S^2}$$

$$\Phi(Z) = \frac{2i\sigma}{4\pi^2\varepsilon_0} \int_{-\infty}^{\infty} \frac{\sin(2\pi Sp)}{S^2} e^{-2\pi iSZ} dS$$

$$= \frac{2i\sigma}{4\pi^2\varepsilon_0} \int_{-\infty}^{\infty} \frac{\sin(2\pi Sp)\cos(2\pi SZ)}{S^2} dS + \frac{2\sigma}{\pi} \int_{-\infty}^{\infty} \frac{\sin(2\pi Sp)\sin(2\pi SZ)}{S^2} dS$$

$$\frac{2i\sigma}{4\pi^2\varepsilon_0} \int_{-\infty}^{\infty} \frac{\sin(2\pi Sp)\cos(2\pi SZ)}{S^2} dS = 0$$

$$\frac{2\sigma}{4\pi^2\varepsilon_0} \int_{-\infty}^{\infty} \frac{\sin(2\pi Sp)\sin(2\pi SZ)}{S^2} dS = \frac{2\pi\sigma}{4\pi\varepsilon_0}\left(-|p-Z| + |p+Z|\right)$$

$$\therefore \Phi(Z) = \frac{\sigma}{2\varepsilon_0}\left(-|p-Z| + |p+Z|\right)$$

between the plates ($-p < Z < p$), $\Phi(Z) = \dfrac{Z\sigma}{\varepsilon_0}$ and $\Delta\Phi = \Phi(p) - \Phi(-p) = \dfrac{2p\sigma}{\varepsilon_0} = \dfrac{d\sigma}{\varepsilon_0}$

For SI calculation, Φ is in volts, d in meters, and σ in C/m^2; when d and σ are Å and charges/Å^2, respectively, the conversion becomes:

$$\Delta\Phi = \Phi(p) - \Phi(-p) = \frac{2p\sigma}{\varepsilon_0} = \frac{d\sigma}{\varepsilon_0}$$

$$\Delta\Phi = \frac{d\left(\times 10^{-10}\right) \times \sigma\left(1.602 \times 10^{-19} \times 10^{20}\right)}{\left(8.854 \times 10^{-12}\right)} = 180.954\, d\sigma$$

$$\sigma\left(\text{charges/Å}^2\right) = 0.005526 \frac{\Delta\Phi(V)}{d(\text{Å})}$$

as before

Capacitor summary (from Edmonds)

basic equations $\Delta\Phi = \frac{Q_{tot} d}{A\varepsilon_0} = \frac{\sigma d}{\varepsilon_0}$; $C_{tot} = \frac{Q_{tot}}{\Delta\Phi} = \frac{A\varepsilon_0}{d}$; $C_s = \frac{C_{tot}}{A} = \frac{\sigma}{\Delta\Phi} = \frac{\varepsilon_0}{d}$

these equations are in SI units. To find charge density (charges/Å^2) that corresponds to a voltage ΔV across a gap d (Å), the following conversion may be employed

$$\sigma = \frac{\varepsilon_0 \Delta\Phi}{d}$$

$$\sigma = \frac{\left(1.602\times10^{-19}\ \text{C/charge}\right)}{\left(10^{-20}\ \text{m}^2/\text{Å}^2\right)} = \frac{\left(8.8542\times10^{-12}\right)\Delta\Phi}{d\left(10^{-10}\ \text{m/Å}\right)}$$

$$\sigma\left(\text{charge/Å}^2\right) = 0.00553\frac{\Delta\Phi\left(\text{volts}\right)}{d\left(\text{Å}\right)}\left(\varepsilon\right)$$

so, a voltage of 1 V across 10 Å corresponds to a charge density of 5.53 x 10^{-4} charge/Å^2. If there is a material of dielectric constant ε, the charge density is multiplied by ε (I think!!).

membrane capacitance, filled with dielectric material with dielectric constant ε

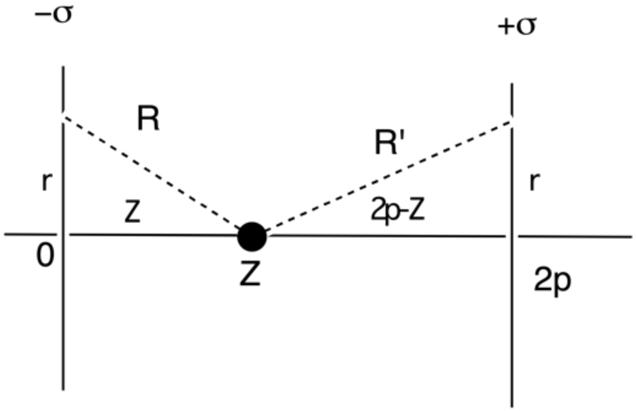
$$C_S = \frac{C_{tot}}{A} = \frac{\sigma}{d} = \frac{\varepsilon\varepsilon_0}{d}$$

for a membrane, $C_s \sim 1\ \mu\text{F cm}^{-2} \sim 0.01\ \text{F m}^{-2}$; 1 F = 1C/1V

$$C_S = \frac{C_{tot}}{A} = \frac{\sigma}{d} = \frac{\varepsilon\varepsilon_0}{d}$$

$$\varepsilon = \frac{dC_S}{\varepsilon_0} = \frac{\left(4\times10^{-9}\ \text{m}\right)\left(1\times10^{-2}\ \text{m}^{-2}\right)}{8.85418782\times10^{-12}\text{C V}^{-1}\ \text{m}^{-1}} \sim 4.5$$

Coulomb's law analysis of parallel plate capacitor



$$d\Phi(Z)=\frac{dq}{R}=\sigma 2\pi r dr\left(\frac{1}{R'}-\frac{1}{R}\right)=\sigma 2\pi r dr\left(\frac{1}{\sqrt{r^2+(2p-Z)^2}}-\frac{1}{\sqrt{r^2+Z^2}}\right)$$

$$\Phi(Z)=2\pi\sigma\int_0^\infty r\,dr\left(\frac{1}{\sqrt{r^2+(2p-Z)^2}}-\frac{1}{\sqrt{r^2+Z^2}}\right)$$

let $u=r^2;\quad a=(2p-Z)^2;\quad b=Z^2$

$$\Phi=\pi\sigma\int_0^\infty du\left(\frac{1}{\sqrt{u+a}}-\frac{1}{\sqrt{u+b}}\right)$$

with $\int_0^\infty du\left(\frac{1}{\sqrt{u+a}}-\frac{1}{\sqrt{u+b}}\right)=2\left(\sqrt{b}-\sqrt{a}\right)$

$$\Phi(Z)=2\pi\sigma\left(\sqrt{b}-\sqrt{a}\right)=2\pi\sigma\left(Z-(2p-Z)\right)$$

$$=2\pi\sigma(2Z-2p)$$

$$\Delta\Phi=\Phi(Z=2p)-\Phi(Z=0)=8\pi\sigma p=4\pi\sigma d$$

where d = full separation between plates.

when units of e and Å are used, the right-hand side is (e/Å) or energy; ΔΦ in volts is then

$$\Delta\Phi=4\pi\sigma d=4\pi\frac{1389}{96.5}\sigma d$$

$$=180.5\sigma d$$

or

$$\sigma\left(\text{charge/Å}^2\right)=\frac{1}{180.5}\frac{\Delta\Phi}{d(\text{Å})}=0.0055\frac{\Delta\Phi}{d}$$

as above.

For a somewhat more complicated system, composed of pairs of planes with charge –σ positioned at ± a, and with charge + σ at ±b (assume b>a), the potential for |z| > b may be found to vanish following the previous derivation:

$$d\Phi(z) = \frac{2\pi r\sigma dr}{4\pi\varepsilon_0}\left[\left(\frac{1}{R_1}\right) - \left(\frac{1}{R_2}\right) - \left(\frac{1}{R_3}\right) + \left(\frac{1}{R_4}\right)\right]$$

$$R_1^2 = (z-b)^2 + r^2$$

$$R_2^2 = (z-a)^2 + r^2$$

$$R_3^2 = (z+a)^2 + r^2$$

$$R_4^2 = (z+b)^2 + r^2$$

Evaluating the integral as above gives

$$\Phi(z) = \frac{\sigma}{2\varepsilon_0}\left[|z+a| + |z-a| - |z+b| - |z+b|\right]$$

for |z| > b, $\Phi(z) = 0$

for |z| < a, $\Phi(z) = \frac{\sigma}{\varepsilon_0}(a-b)$ $(= 180.954\sigma(a-b))$

for a < |z| < b, $\Phi(z) = \frac{\sigma}{\varepsilon_0}(z-b)$

in finite_difference_test.nb, with s = -0.000553, a = 3 Å and b = 5A, the potential for |z| < a is calculated to be 0.2000V from the above formula, consistent with the calculation (setting Φ=0 outside the outer plates).

Asymptotic value for potential at center of two oppositely oriented “dipole” planes

Given two infinite and identical charged planar surfaces of charge density σ (approximated as a Gaussian of width A, with the positive (say) planes at +/-a and the negative at +/- b ,where b-p = x (small with respect to p).

The Fourier transform of the charge distribution is

$$2\sigma\cos\left(2\pi Sa\right)e^{-\left(\pi SA\right)^2} - 2\sigma\cos\left(2\pi Sb\right)e^{-\left(\pi SA\right)^2}$$

so the potential is given by

$$\Phi\left(z\right) = \frac{2\sigma}{4\pi^2\varepsilon_0}\int_0^\infty \frac{\left(\cos\left(2\pi Sa\right) - \cos\left(2\pi Sb\right)\right)e^{-\left(\pi SA\right)^2}}{S^2} e^{-2\pi iSz}dz$$

at z=0, $\Phi\left(0\right) = \frac{2\sigma}{4\pi^2\varepsilon_0}\left[2\pi^2 b\,\mathrm{Erf}\frac{b}{A} - 2\pi^2 p\,\mathrm{Erf}\frac{a}{A} + 2\pi^{3/2}\left(e^{-b^2/A^2} - e^{-a^2/A^2}\right)\right]$

with b = p+x and small x, this may be expanded to give

$$\Phi\left(0\right) = \frac{2\sigma}{4\pi^2\varepsilon_0}\left[\left(\frac{8\pi^{3/2}p}{A}e^{-a^2/A^2} + 2\pi^2\,\mathrm{Erf}\frac{a}{A}\right)x\right]$$

and the limit becomes

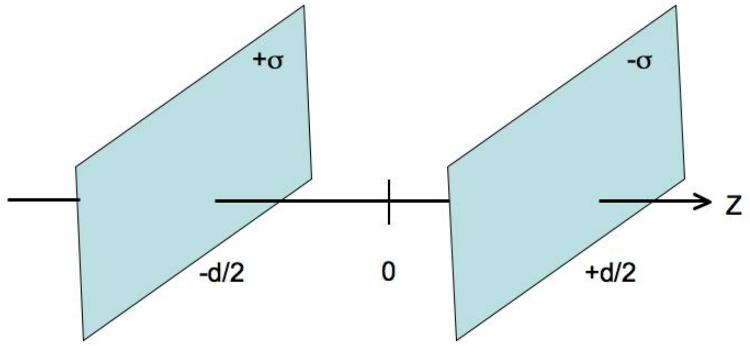
$$\lim_{\frac{p}{A}\to\infty}\Phi\left(0\right) = \frac{2\sigma}{4\pi^2\varepsilon_0}\left[2\pi^2 x\right] = \frac{\sigma x}{\varepsilon_0} = \frac{\sigma\left(b-a\right)}{\varepsilon_0}$$

as above

reciprocal space solution to parallel plate capacitor

original December 2008?

parallel plate part by inverse FT updated 8/15/2012



for the continuum case, let h, k, l be the components of S along x, y, z.

$$F(hkl) = \iiint \rho(xyz) e^{2\pi i(hx+ky+lz)} dxdydz$$

$$= \sigma \iint e^{2\pi i(hx+ky)} dxdy \left[e^{2\pi i\left(-l\frac{d}{2}\right)} - e^{2\pi i\left(l\frac{d}{2}\right)} \right]$$

$$F(00l) = \sigma\left[e^{-\pi ild} - e^{\pi ild} \right]$$

$$= -2i\sigma \sin(\pi ld)$$

note: $F(hkl) = 0$ for $h \neq 0$ or $k \neq 0$ since $\iint e^{2\pi i(hx+ky)} dxdy = \delta(h)\delta(k)$

(so $h^2+k^2+l^2 = l^2$ for non-zero $F(hkl)$in inverse FT for $\Phi(z)$)

$$\Phi(z) = \int_{-\infty}^{\infty} \frac{F(00l)}{\pi l^2} e^{-2\pi ilz} dl = -2i\sigma \int_{-\infty}^{\infty} \frac{\sin(\pi ld)}{\pi l^2} e^{-2\pi ilz} dl$$

$$= -\frac{2i\sigma}{\pi} \int_0^{\infty} \frac{\sin(\pi ld)}{l^2} \left(e^{-2\pi ilz} - e^{2\pi ilz} \right) dl = -\frac{4\sigma}{\pi} \int_0^{\infty} \frac{\sin(\pi ld)\sin(2\pi lz)}{l^2} dl$$

$$= -\frac{4\sigma}{\pi} \frac{(2\pi z)\pi}{2} = -4\sigma\pi z$$

where the last amazing integral comes from Gradshteyn & Rhyzik 3.741.3

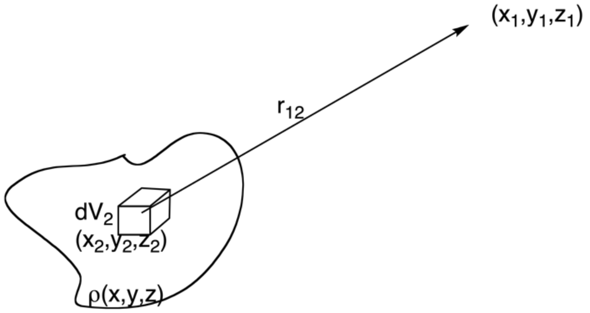
$$\int_0^{\infty} \frac{\sin(ax)\sin(bx)}{x^2} dx = \frac{a\pi}{2} \quad [0 < a \leq b];$$

$$= \frac{b\pi}{2} \quad [0 < b \leq a].$$

so the potential decreases linearly with z and the total potential drop is $4\sigma\pi d$, as derived previously.

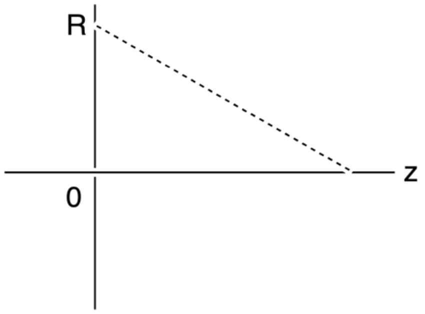
Electric field near a uniform sheet of charge (Feynman II 4.18)

- note: this is a uniform sheet of charge, not a sheet of charge on a conductor II 5-4:5-8!!



$$E_x\left(x_1,y_1,z_1\right)=\frac{1}{4\pi\varepsilon_0}\int\frac{\left(x_1-x_2\right)\rho\left(x_2,y_2,z_2\right)dx_2dy_2dz_2}{\left(\left(x_1-x_2\right)^2+\left(y_1-y_2\right)^2+\left(z_1-z_2\right)^2\right)^{3/2}},\text{ etc}$$

for the electric field along the z axis:



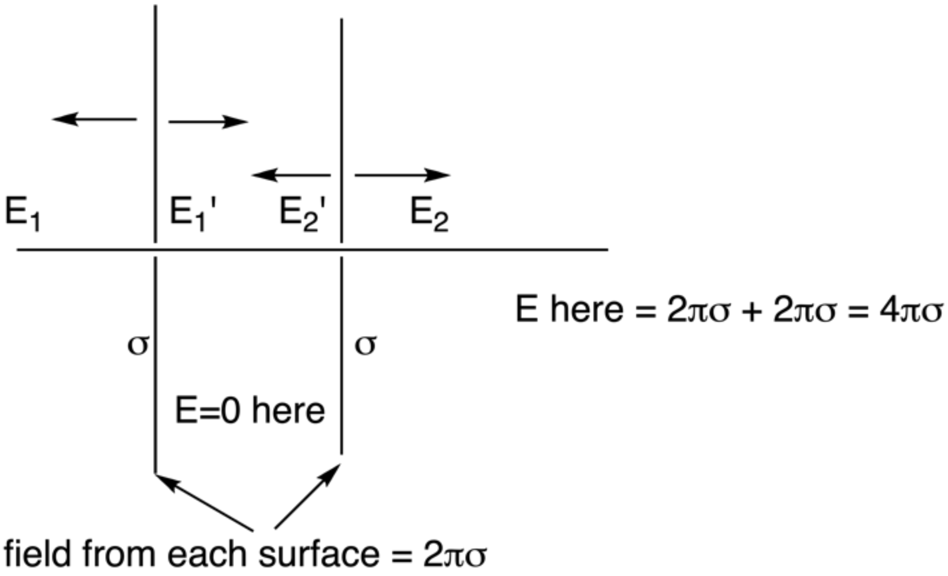
$$E_z=\int_0^\infty\frac{z2\pi R\sigma dR}{\left(R^2+z^2\right)^{3/2}}=z\pi\sigma\int_0^\infty\frac{2RdR}{\left(R^2+z^2\right)^{3/2}}$$

let u = R^2 and a = z^2:

$$\begin{aligned}E_z&=\int_0^\infty\frac{z2\pi R\sigma dR}{\left(R^2+z^2\right)^{3/2}}=z\pi\sigma\int_0^\infty\frac{2RdR}{\left(R^2+z^2\right)^{3/2}}\\&=z\pi\sigma\int_0^\infty\frac{du}{\left(u+a\right)^{3/2}}=z\pi\sigma\left(-\frac{2}{\sqrt{a+u}}\Big|_0^\infty\right)=z\pi\sigma\left(0+\frac{2}{\sqrt{a}}\right)\\&=2\pi\sigma\end{aligned}$$

and $$E_x=\int_0^\infty\frac{x\sigma 2\pi\left(x^2+y^2\right)^{1/2}dxdy}{\left(R^2+x^2+y^2\right)^{3/2}}=E_y=0$$

for a charged conductor, each of the two surfaces gives an electric field of $2\pi\sigma = 4\,\pi\sigma$ total


E_1
E_1'
E_2'
E_2
E here = $2\pi\sigma + 2\pi\sigma = 4\pi\sigma$
σ
σ
E=0 here
field from each surface = $2\pi\sigma$

Linearized Poisson-Boltzmann Equation for Planar Systems

$$\nabla^2\Phi = \frac{-4\pi\rho}{\varepsilon} = \kappa^2\Phi \quad \left(\kappa^2 = \frac{8\pi e^2 N_A I}{1000\varepsilon kT}\right)$$

$$\rho = -\frac{\varepsilon\kappa^2\Phi}{4\pi}$$

planar system (Gouy-Chapman)

the PB equation $\nabla^2\Phi = \kappa^2\Phi$ has the solution $\Phi = Ae^{-\kappa z}$; to determine the value of A, the electroneutrality condition can be applied:

$$\sigma = -\int_0^\infty \rho(z)dz = +\frac{\kappa^2\varepsilon}{4\pi}A\int_0^\infty e^{-\kappa z}dz = \frac{\kappa\varepsilon}{4\pi}A$$

$$A = \frac{4\pi\sigma}{\kappa\varepsilon}$$

giving

$$\Phi(z) = \frac{4\pi\sigma}{\kappa\varepsilon}e^{-\kappa z}$$

in the vicinity of the surface, the potential varies with distance Δ as:

$$\Phi(\Delta) - \Phi(0) = \frac{4\pi\sigma}{\kappa\varepsilon}\left((1-\kappa\Delta)-1\right) = -\frac{4\pi\sigma\Delta}{\varepsilon}$$

for small distances, the surface of a large sphere should also look planar;

for the Debye Huckel system with the screened Coulomb potential $\Phi(r) = \frac{ze}{\varepsilon}\frac{e^{\kappa a}}{(1+\kappa a)}\frac{e^{-\kappa r}}{r}$

$$
\begin{aligned}
\Phi(a+\Delta)-\Phi(a) &= \frac{ze}{\varepsilon}\frac{e^{\kappa a}}{(1+\kappa a)}\left[\frac{e^{-\kappa a}e^{-\kappa\Delta}}{a\left(1+\frac{\Delta}{a}\right)}-\frac{e^{-\kappa a}}{a}\right] \\
&= \frac{ze}{\varepsilon a}\frac{1}{(1+\kappa a)}\left[(1-\kappa\Delta)\left(1-\frac{\Delta}{a}\right)-1\right] \\
&= \frac{ze}{\varepsilon a}\frac{1}{(1+\kappa a)}\left[1-\kappa\Delta-\frac{\Delta}{a}+\kappa\frac{\Delta^2}{a}-1\right] \\
&= -\frac{ze}{\varepsilon a}\frac{\Delta}{(1+\kappa a)}\left(\kappa+\frac{1}{a}\right) \\
&= -\frac{ze}{\varepsilon a^2}\frac{\Delta}{(1+\kappa a)}(\kappa a+1) = -\frac{ze}{\varepsilon a^2}\Delta \\
&= \text{-}\frac{4\pi\sigma\Delta}{\varepsilon}\left(\text{with } \sigma=\frac{ze}{4\pi a^2}\right)
\end{aligned}
$$

and for the reference Coulombic system, for a sphere of radius a and total charge Q:

$$
\Phi(r)=\frac{Q}{\varepsilon r}=\frac{4\pi a^2\sigma}{\varepsilon r} \quad (r \geq a)
$$

the variation in potential near the surface is:

$$
\Phi(a+\Delta)-\Phi(a)=\frac{4\pi a^2\sigma}{\varepsilon}\left[\frac{1}{a+\Delta}-\frac{1}{a}\right]=\frac{4\pi a^2\sigma}{a\varepsilon}\left[1-\frac{\Delta}{a}-1\right]=-\frac{4\pi\sigma\Delta}{\varepsilon}
$$

in all these cases, the electric field is given by $E=-\frac{\partial\Delta\Phi}{\partial\Delta}=\frac{4\pi\sigma}{\varepsilon}$.

Gouy Chapman theory (see Chapter 12 of D.T. Edmonds)

In a solution of dielectric constant ε adjacent to a planar membrane, Poisson's equation is

$$\frac{d^2\Phi(z)}{dz^2} = -\frac{\rho(z)}{\varepsilon\varepsilon_0}$$

with the electric field $E(z) = -\frac{d\Phi(z)}{dz}$.

Using Boltzmann's equation

$$\rho(z) = \sum_i z_i q n_i \exp\left[-\frac{z_i q\Phi(z)}{kT}\right]$$

$$\frac{d^2\Phi(z)}{dz^2} = -\sum_i \frac{z_i q n_i}{\varepsilon\varepsilon_0}\exp\left[-\frac{z_i q\Phi(z)}{kT}\right]$$

This may be solved using the following derivative identity

$$\frac{d^2\Phi(z)}{dz^2} = \frac{1}{2}\frac{d}{d\Phi}\left[\frac{d\Phi(z)}{dz}\right]^2$$

$$\text{and } F(\Phi) = \int_\Phi \frac{d}{d\Phi}\left[F(\Phi)\right]d\Phi \text{ with } F(\Phi) = \left[\frac{d\Phi(z)}{dz}\right]^2$$

$$\int_\Phi \frac{d}{d\Phi}\left[\frac{d\Phi(z)}{dz}\right]^2 d\Phi = \left[\frac{d\Phi(z)}{dz}\right]^2 = 2\int \frac{d^2\Phi(z)}{dz^2}d\Phi$$

$$\left[\frac{d\Phi(z)}{dz}\right]^2 = -2\sum_i \left(\frac{z_i q n_i}{\varepsilon\varepsilon_0}\right)\int_{\Phi=0}^{\Phi=\Phi(z)} \exp\left[-\frac{z_i q\Phi(z)}{kT}\right]d\Phi$$

$$\int_{\Phi=0}^{\Phi=\Phi} \exp\left[-\alpha\Phi\right]d\Phi = -\frac{1}{\alpha}\left(\exp\left[-\alpha\Phi\right]-1\right)$$

$$E^2(x) \equiv \left[\frac{d\Phi(z)}{dz}\right]^2 = \frac{2kT}{\varepsilon\varepsilon_0}\sum_i n_i\left(\exp\left[-\frac{z_i q\Phi(z)}{kT}\right]-1\right)$$

$$E(0) = \frac{D(0)}{\varepsilon\varepsilon_0} = \frac{\sigma_s}{\varepsilon\varepsilon_0}$$

$$\sigma_s^2 = 2kT\varepsilon\varepsilon_0\sum_i n_i\left(\exp\left[-\frac{z_i q\Phi(0)}{kT}\right]-1\right)$$

For a symmetric electrolyte, expanding the exponential $\exp[x] = 1 + x + x^2/2 + \ldots$ gives for a symmetric electrolyte (1:1, 2:2, etc). (with 2 different definitions of “z”: valence charge and distance from interface…..)

$$E^2(x) = \frac{2kT}{\varepsilon\varepsilon_0}\sum_i n_i\left(\exp\left[-\frac{z_i q\Phi(z)}{kT}\right] - 1\right) = \frac{2n}{\varepsilon\varepsilon_0 kT}\left(zq\Phi(z)\right)^2$$

$$E(z) = -\frac{d\Phi(z)}{dz} = \left(\frac{2n}{\varepsilon\varepsilon_0 kT}\right)^{1/2} q\Phi(z)$$

$$-\frac{d\Phi(z)}{dz} = \frac{\Phi(z)}{\lambda}\left(\text{for a 1:1 electrolyte}\right)$$

$$\text{with } \left(\frac{1}{\lambda}\right)^2 = \frac{2nq^2}{\varepsilon\varepsilon_0 kT}$$

the solution to this differential equation has an exponential fall off with distance from the interface:

$$\Phi(z) = \Phi(0)\exp\left[-z/\lambda\right]$$

Finite Difference Solutions to the Poisson Equation

July 2010

Poisson's equation for a heterogeneous dielectric material may be described:

$$-\nabla\varepsilon(r)\cdot\nabla\phi(r)=\frac{\rho(r)}{\varepsilon_0}$$

with the following boundary conditions for a one-dimensional system (along z)

$\phi(z)$ is continuous

$\varepsilon(z)\frac{\partial\phi(z)}{\partial z}$ is continuous across an interface

it may also be appropriate to set $\phi(z)=0$ at some point.

If the system is sampled on a grid with spacing h, the derivatives may be approximated:

$$\varepsilon_+\cdot\nabla\phi_+\sim\frac{(\varepsilon_{i+1}+\varepsilon_i)}{2}\left(\frac{\phi_{i+1}-\phi_i}{h}\right)$$

$$\varepsilon_-\cdot\nabla\phi_-\sim\frac{(\varepsilon_{i-1}+\varepsilon_i)}{2}\left(\frac{\phi_i-\phi_{i-1}}{h}\right)$$

$$-(\nabla\varepsilon\cdot\nabla\phi)_i\sim-\frac{\varepsilon\cdot\nabla\phi_+}{h}-\frac{\varepsilon\cdot\nabla\phi_-}{h}\sim-\frac{(\varepsilon_{i+1}+\varepsilon_i)}{2}\left(\frac{\phi_{i+1}-\phi_i}{h^2}\right)-\frac{(\varepsilon_{i-1}+\varepsilon_i)}{2}\left(\frac{\phi_i-\phi_{i-1}}{h^2}\right)$$

if the ρ_i are known, the ϕ_i may be obtained as solutions to the matrix equation

$$A\phi=\frac{1}{\varepsilon_0}\rho$$

A is a banded diagonal matrix with elements

$$A_{ii}=\frac{(\varepsilon_{i+1}+\varepsilon_{i-1})}{2}+\varepsilon_i,\ A_{i,i-1}=-\frac{(\varepsilon_i+\varepsilon_{i-1})}{2},\ A_{i,i+1}=-\frac{(\varepsilon_i+\varepsilon_{i+1})}{2}$$

At the boundaries (the first and last grid points), if the dielectric constant in those regions is a constant (as it should be), then

$$A_{11}=\varepsilon_1+\varepsilon_2,\quad A_{12}=-(\varepsilon_1+\varepsilon_2)$$

$$A_{NN}=\varepsilon_{N-1}+\varepsilon_N,\quad A_{12}=-(\varepsilon_{N-1}+\varepsilon_N)$$

Matrix *A* has a determinant of 0, however and cannot be inverted, so a constraint needs to be introduced – typically either that the sum of the (appropriately weighted) ϕ_i add to zero (ie – if a point is on a mirror plane, its weight is 0.5, etc), or that the potential has a specified value at a certain point (ie – $\phi_N = 0$). The constraint coefficients can go on the last row of A, with the corresponding value of the constraint equation placed in the last element of the ρ vector).

The Membrane Dipole Potential – evaluation from x-ray and neutron diffraction data?

this section is a work in progress

M.C. Wiener and S.H. White Biophysical J. 61, 434-447 (1992)

The membrane dipole potential is thought to arise from the orientation of dipoles in the sidechainand glycerol backbone of phospholipids, generating a potential of ~+100 to +1000 mV in the interior of the membrane bilayer. More detailed discussions may be found in
R.J. Clarke, Adv. Coll. Interface Sci. 89, 263 (2001)
L. Wang, P.S. Bose and F.J. Sigworth, PNAS 103, 18528 (2006) (use of cryoEM)

The eventual goal of this section is to see whether electrostatic calculations based on experimental measurements by Wiener and White of x-ray and neutron diffraction from the liquid crystalline (Lα phase) bilayer of DOPC, sensitive to the electron and nuclear distributions, respectively, can be used to calculate the membrane dipole potential in this system.

DOPC = 1,2-dioleoly-*sn*-glycero-3-phosphocholine – composition $C_{44}H_{84}NO_8P$ per phospholipid = 434 protons/electrons
+5.36 waters (x 10 electrons/water) =53.6 to give 487.68 protons/electrons per PL x 2 = 975.2 protons/electrons per bilayer

d spacing (normal to bilayer) = 49.1 Å
area/PL = 59.3 Å^2 (WW); 72 Å^2 (Nagle), 70 Å^2 (Engelman)
(note: these values are somewhat different than used in original Mathematica spreadsheets)

group (del numbering)	N (per PL)	Z (Å)	A (Å) 1/e halfwidth	total protons
CH_3	2	0	2.95	18
iCH_2 (1)	2.74	2.97	2.74	21.92
mCH_2 (2)	8.51	5.60	4.21	68.08
oCH_2 (3)	16.75	12.85	5.14	134.0
C=C (8)	2	7.88	4.29	28
CO_2 (4)	2	15.97	2.73	44
glyc (5)	1	18.67	2.37	23
PO_4 (6)	1	20.19	3.08	47
CHOL (7)	1	21.89	3.48	50
water (9)	5.36	22.51	4.63	42.88

$$n_i(z) = \frac{N_i}{A_i\sqrt{\pi}} e^{-((z-Z_i)/A_i)^2}$$

$$1 = \frac{1}{A\sqrt{\pi}} \int_{-\infty}^{\infty} e^{-(z/A)^2} dz \quad \text{(normalization)}$$

$$e^{-(\pi SA)^2} = \frac{1}{A\sqrt{\pi}} \int_{-\infty}^{\infty} e^{-(z/A)^2} \cos(2\pi Sz) dz \quad \text{(FT)}$$

$$\frac{1}{A\sqrt{\pi}} e^{-(z/A)^2} = 2\int_{0}^{\infty} e^{-(\pi SA)^2} \cos(2\pi Sz) dS \quad \text{(inverse FT)}$$

when there are symmetric peaks at ±Z, the FT = $2\cos(2\pi SZ)e^{-(\pi SA)^2}$

and when there are N groups (protons, electrons) the overall scattering factor contribution are:

$$2N\cos(2\pi SZ)e^{-(\pi SA)^2}$$

X-ray and neutron diffraction measurements from stacked bilayers (include the use of b_x, b_N)

index	Fobs (x-ray)	Fcalc (x-ray)	Fobs (neutron)	Fcalc (neutron)
0		275.16		6.06
1	-43.95	-43.98	-8.00	-7.15
2	-0.52	-0.64	-4.51	-4.41
3	5.15	5.34	4.81	4.61
4	-11.97	-12.15	-5.18	-5.36
5	3.38	3.77	-0.59	-0.49
6	-2.47	-2.80	0.84	0.80
7	2.03	2.05	0.0	-00.5
8	-2.24	-1.94	-0,94	-0.91

Table 1 has X-ray scattering lengths in units of 10^{-12} cm and "are given by the electron number multiplied by mc^2/e^2" It seems to me that these are divided by mc^2/e^2 – for example, 275.16 * 3.55 = 976.82 ~ 975.2 expected number of electrons.

In cgs units $m=9.11\text{x}10^{-28}$ gm, $c=2.998\text{x}10^{10}$ cm/sec, $e = 4.8\text{x}10^{-10}$ esu, so that $mc^2/e^2 = 3.55 \text{ x } 10^{+12}$ (cm^{-1}). With 9 electrons for CH_3, dividing by 3.55 gives 2.5352, very close to the entry in Table 1 (2.540). Looking at the agreement between Fobs and Fcalc from the above model, it seems that the scale factor is very close to 3.55.

In Figure 2B, when the ordinate is divided by 16.73 (= 59.3/3.55 – haven't figured out the exponents yet) to convert to e/Å^3, the minimum and maximum are ~ 0.21 and 0.47, with the interbilayer trough = 0.38.