

The Polarizable Continuous Solvation Model

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Abstract

In this handout, I will go through the polarizable continuous solvation model developed by Tomasi, Cammi, Mennucci, Cossi, Barone, and Chipman et al. I will try sticking to the Gaussian unit.

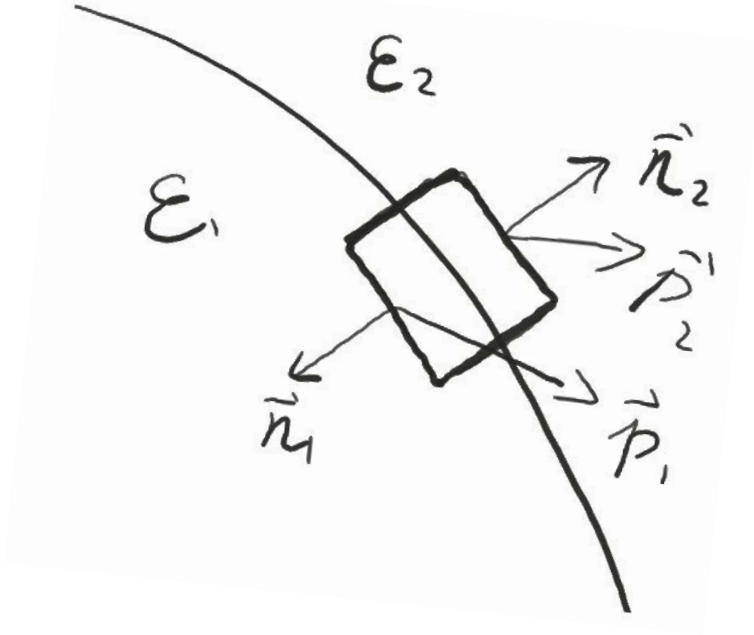
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I. INTRODUCTION

The polarizable continuum solvation model (PCM), also known as apparent surface charge (ASC) approach, was developed by Tomasi et al more than three decades ago, and was continuously refined by many others as well as Tomasi himself. It has several variants, such as D-PCM[Miertus,1981], C-PCM[Barone,1998] and IEF-PCM[Cances,1997]. Nowadays, the most widely used variant of PCM methods is IEF-PCM.

II. METHODS

In this model, the whole space is separated in to two (can be more than two) regions. One region is characterized by a dielectric constant $\epsilon_1 = 1$, where the solute resides. The other region has a dielectric constant ϵ_2 , which is a continuous representation of the solvent molecules. For simplicity, ϵ_1 will not appear in the following, and we set $\epsilon = \epsilon_2$.



At the dielectric boundary, a σ charge distribution appears, because of the discontinuity of the dielectric constant, which can be expressed in terms of the difference of the respective polarization density \mathbf{P}_1 and \mathbf{P}_2 by

$$\sigma_{12} = -(\mathbf{P}_2 - \mathbf{P}_1) \cdot \mathbf{n}_{12}, \quad (1)$$

in which

$$\mathbf{P}_i = -\frac{\epsilon_i - 1}{4\pi} \nabla \phi. \quad (2)$$

In the inner region, $\mathbf{P}_1 = 0$, due to $\epsilon_1 = 1$. Therefore,

$$\sigma = -\mathbf{P} \cdot \mathbf{n} = \frac{\epsilon - 1}{4\pi} \nabla \phi_{\mathbf{S}^+} \cdot \mathbf{n} = \frac{\epsilon - 1}{4\pi\epsilon} \nabla \phi_{\mathbf{S}^-} \cdot \mathbf{n}. \quad (3)$$

It is more convenient to calculate the electric field at the inner surface of the cavity. Here, $\phi_{\mathbf{S}^-}$ has two sources

$$\phi_{\mathbf{S}^-} = \phi_{\mathbf{S}^-}^{\rho} + \phi_{\mathbf{S}^-}^{\sigma}, \quad (4)$$

which are the contributions from the solute and the polarized charge on the interface. The formal one can be written as

$$\phi^{\rho}(\mathbf{r}) = \iiint_{\mathbf{V}} \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}'. \quad (5)$$

Here, we have omitted the subscript \mathbf{S}^- , and \mathbf{V} is the region enclosed by surface \mathbf{S} . Associated with this potential is an electric field given by $-\nabla\phi^{\rho}(\mathbf{r})$. The negative of the normal component of this field at any point on the surface $\mathbf{\Gamma}$ is given by

$$\partial\phi^{\rho}(\mathbf{s}) = \iiint_{\mathbf{V}} \rho(\mathbf{r}') \frac{\partial}{\partial \mathbf{n}_{\mathbf{s}}} \frac{1}{|\mathbf{s} - \mathbf{r}'|} d^3\mathbf{r}', \quad (6)$$

where $\mathbf{n}_{\mathbf{s}}$ is a unit vector parallel to the outward-directed normal at point \mathbf{s} on $\mathbf{\Gamma}$. Similarly, the second term can be expressed as

$$\phi^{\sigma}(\mathbf{r}) = \oint_{\mathbf{\Gamma}} \frac{\sigma(\mathbf{s}')}{|\mathbf{r} - \mathbf{s}'|} d^2\mathbf{s}'. \quad (7)$$

It is convenient to define certain operators that act only over the surface $\mathbf{\Gamma}$. The operator \mathcal{S} acting on a given surface function (e.g. charge distribution) $\sigma(\mathbf{s})$ produces the corresponding surface charge potential at the point \mathbf{s} on $\mathbf{\Gamma}$, i.e.,

$$\mathcal{S}\sigma(\mathbf{s}) = \oint_{\mathbf{\Gamma}} \sigma(\mathbf{s}') \frac{1}{|\mathbf{s} - \mathbf{s}'|} d^2\mathbf{s}'. \quad (8)$$

The operator \mathcal{D}^* acting on a given surface function $\sigma(\mathbf{s})$ produces the negative of the outward-directed normal component of the electric field at the surface from $\phi^{\sigma}(\mathbf{s})$, i.e.,

$$\mathcal{D}^*\sigma(\mathbf{s}) = \oint_{\mathbf{\Gamma}} \sigma(\mathbf{s}') \frac{\partial}{\partial \mathbf{n}_{\mathbf{s}}} \frac{1}{|\mathbf{s} - \mathbf{s}'|} d^2\mathbf{s}'. \quad (9)$$

Note that the contribution of the charge on \mathbf{s} itself has not been counted for. Thus, the corresponding negative of the outward-directed normal component of the electric field at a point \mathbf{s}^{int} on the interior face of Γ is $\mathcal{D}^*\sigma(\mathbf{s}) + 2\pi\sigma(\mathbf{s})$, while at a point \mathbf{s}^{ext} on the exterior face of Γ it is $\mathcal{D}^*\sigma(\mathbf{s}) - 2\pi\sigma(\mathbf{s})$. The closely related operator \mathcal{D} acting on a given surface function $\sigma(\mathbf{s})$ produces the corresponding surface dipole or double layer potential on Γ , i.e.,

$$\mathcal{D}\sigma(\mathbf{s}) = \iint_{\Gamma} \sigma(\mathbf{s}') \frac{\partial}{\partial \mathbf{n}_{\mathbf{s}'}} \frac{1}{|\mathbf{s} - \mathbf{s}'|} d^2\mathbf{s}'. \quad (10)$$

I do not quite understand the physical meaning of operator \mathcal{D} . What is surface dipole or double layer potential?

This potential is also discontinuous across Γ , and at a point \mathbf{s}^{int} is $\mathcal{D}\sigma(\mathbf{s}) - 2\pi\sigma(\mathbf{s})$ while at a point \mathbf{s}^{ext} is $\mathcal{D}\sigma(\mathbf{s}) + 2\pi\sigma(\mathbf{s})$. Note that in general

$$\mathcal{D}S\sigma(\mathbf{s}) = S\mathcal{D}^*\sigma(\mathbf{s}). \quad (11)$$

In fact, the solute electrons are not completely enclosed by the dielectric surface, some portion of the electrons may inevitably penetrate into the bulk region of the dielectric and cause volume polarization. It also follows the Gauss's law as given by

$$\beta(\mathbf{r}) = -\frac{\epsilon - 1}{\epsilon} \rho^{ext}(\mathbf{r}), \quad (12)$$

which contributes $\phi^\beta(\mathbf{s})$ and $-\nabla\phi^\beta(\mathbf{s})$ to the total potential and electric field on the point \mathbf{s} on Γ . For the potential, we also have

$$\phi^\beta(\mathbf{r}) = -\frac{\epsilon - 1}{\epsilon} \phi^{\rho^{ext}}(\mathbf{r}). \quad (13)$$

Now we rewrite Eq. 3 as

$$\sigma(\mathbf{s}) = -\frac{\epsilon - 1}{4\pi\epsilon} [-\partial\phi^\rho - \partial\phi^\beta - \mathcal{D}^*\sigma(\mathbf{s}) - 2\pi\sigma(\mathbf{s})] \quad (14)$$

or

$$\mathcal{F}\sigma(\mathbf{s}) = \left(\frac{\epsilon - 1}{\epsilon + 1} \right) \frac{1}{2\pi} [\partial\phi^\rho(\mathbf{s}) + \partial\phi^\beta(\mathbf{s})], \quad (15)$$

with operator \mathcal{F} defined as

$$\mathcal{F} = \mathcal{I} - \left(\frac{\epsilon - 1}{\epsilon + 1} \right) \frac{1}{2\pi} \mathcal{D}^*.$$

Chipman[Chipman,1999] have pointed out that the effect of this volume polarization term can be closely simulated by a certain additional surface polarization charge density $\alpha(\mathbf{s})$, such that

$$\mathcal{S}\alpha(\mathbf{s}) = \phi^\beta(\mathbf{s}) \quad (16)$$

and

$$\partial\phi^\beta(\mathbf{s}) = \mathcal{D}^*\alpha(\mathbf{s}) + 2\pi\alpha(\mathbf{s}) \quad (17)$$

for all points \mathbf{s} on Γ , then it is easily shown that $\phi^\alpha(\mathbf{r}) = \phi^\beta(\mathbf{r})$ for all \mathbf{r} inside as well as on Γ . Applying \mathcal{F} to $\alpha(\mathbf{s})$, we obtain

$$\mathcal{F}\alpha(\mathbf{s}) = \left(\frac{\epsilon-1}{\epsilon+1}\right) \left[\left(\frac{\epsilon}{\epsilon-1}\right) 2\alpha(\mathbf{s}) - \frac{1}{2\pi} \partial\phi^\beta(\mathbf{s}) \right]. \quad (18)$$

Operating on both sides with \mathcal{S} then gives

$$\mathcal{S}\mathcal{F}\alpha(\mathbf{s}) = \left(\frac{\epsilon-1}{\epsilon+1}\right) \left[\left(\frac{\epsilon}{\epsilon-1}\right) 2\phi^\beta(\mathbf{s}) - \frac{1}{2\pi} \mathcal{S}\partial\phi^\beta(\mathbf{s}) \right]. \quad (19)$$

Through judicious application of Green's theorem, at any point \mathbf{r} inside Γ the contribution to the potential $\phi^\rho(\mathbf{r})$ arising from charge density $\rho^{ext}(\mathbf{r})$ lying outside Γ can be represented from knowledge of just $\phi^\rho(\mathbf{s})$ and $\partial\phi^\rho(\mathbf{s})$ on Γ via[Chipman,2000]

$$\phi^{\rho^{ext}}(\mathbf{r}) = \frac{1}{4\pi} \oint\!\!\!\oint_{\Gamma} \left[\partial\phi^\rho(\mathbf{s}') \left\{ \frac{1}{|\mathbf{r}-\mathbf{s}'|} \right\} - \phi^\rho(\mathbf{s}') \left\{ \frac{\partial}{\partial \mathbf{n}_{\mathbf{s}'}} \frac{1}{|\mathbf{r}-\mathbf{s}'|} \right\} \right] d^2\mathbf{s}'. \quad (20)$$

This is a direct consequence of Eq. 1.36 in Jackson's *Classical Electrodynamics, Third Edition*, where the first term in the r.h.s. of this equation is zero due that here we only count the contribution from the penetrated charge into the volume.[JacksonClassicalElectrodynamics1998]

Evaluating this at a point $\mathbf{r} = \mathbf{s}^{int}$ and extending to the corresponding point \mathbf{s} on Γ by taking into account the discontinuity of the last term, we obtain

$$\phi^{\rho^{ext}}(\mathbf{s}) = \frac{1}{2}\phi^\rho(\mathbf{s}) - \frac{1}{4\pi}\mathcal{D}\phi^\rho(\mathbf{s}) + \frac{1}{4\pi}\mathcal{S}\partial\phi^\rho(\mathbf{s}) \quad (21)$$

and

$$\phi^\beta(\mathbf{s}) = -\left(\frac{\epsilon-1}{\epsilon}\right) \left[\frac{1}{2}\phi^\rho(\mathbf{s}) - \frac{1}{4\pi}\mathcal{D}\phi^\rho(\mathbf{s}) + \frac{1}{4\pi}\mathcal{S}\partial\phi^\rho(\mathbf{s}) \right]. \quad (22)$$

Taking it into Eq. 19, we obtain

$$\mathcal{S}\mathcal{F}\alpha(\mathbf{s}) = \left(\frac{\epsilon-1}{\epsilon+1}\right) \left[-\phi^\rho(\mathbf{s}) + \frac{1}{2\pi}\mathcal{D}\phi^\rho(\mathbf{s}) - \frac{1}{2\pi}\mathcal{S}\partial\phi^\rho(\mathbf{s}) - \frac{1}{2\pi}\mathcal{S}\partial\phi^\beta(\mathbf{s}) \right]. \quad (23)$$

Applying \mathcal{S} to Eq. 15 and adding it to Eq. 23, we find

$$\mathcal{SF}\sigma^{SS(V)PE}(\mathbf{s}) = \mathcal{SF}(\sigma(\mathbf{s}) + \alpha(\mathbf{s})) = \left(\frac{\epsilon - 1}{\epsilon + 1}\right) \left[-\phi^\rho(\mathbf{s}) + \frac{1}{2\pi}\mathcal{D}\phi^\rho(\mathbf{s})\right]. \quad (24)$$

You may easily find that in conductor with $\epsilon \rightarrow \infty$, Eq. 24 becomes

$$\mathcal{S}\sigma^{SS(V)PE}(\mathbf{s}) = -\phi^\rho(\mathbf{s}), \quad (25)$$

indicating that the polarized charges cancel the electrostatic potential generated by the solute.

In practice, the surface Γ is discretized into tesserae characterized by its surface area a_i and its center \mathbf{s}_i . The operator acting on this surface should be changed accordingly.[Cossi,2001] If \hat{O} is an operator acting on function f in point \mathbf{s}_i , its finite element counterpart is

$$\hat{O}f(\mathbf{s}_i) \leftrightarrow (\mathbf{O}\mathbf{A}\mathbf{f})_i = \sum_j^{tesserae} O_{ij}a_j f(\mathbf{s}_j), \quad (26)$$

where \mathbf{A} is a diagonal matrix collecting the area of tesserae, \mathbf{O} is the matrix associated to operator \hat{O} , and column vector \mathbf{f} collects the value of f evaluated in the center of tesserae. The surface charge density σ' is substituted by N_{TS} point charges, $q_i = a_i\sigma'(\mathbf{s}_i)$, and the above operators are represented by $N_{TS} \times N_{TS}$ matrices,

$$\mathcal{S}\sigma(\mathbf{s}) \leftrightarrow (\mathbf{S}\mathbf{q})_i = \sum_j S_{ij}q_j$$

$$\mathcal{D}^*\sigma(\mathbf{s}) \leftrightarrow (\mathbf{D}^*\mathbf{q})_i = \sum_j D_{ij}^*q_j$$

$$\mathcal{D}\sigma(\mathbf{s}) \leftrightarrow (\mathbf{D}\mathbf{q})_i = \sum_j D_{ij}q_j$$

where column vector \mathbf{q} collects the solvation charges. Matrix \mathbf{S} has elements

$$S_{ii} = 1.07\sqrt{\frac{4\pi}{a_i}}$$

$$S_{ij} = \frac{1}{|\mathbf{s}_i - \mathbf{s}_j|}$$

The diagonal term follows Klamt.[Klamt,1993] Matrix \mathbf{D}^* has elements

$$D_{ii}^* = -\left(2\pi + \sum_{j \neq i} D_{ji}^*a_j\right) \frac{1}{a_i}$$

$$D_{ij}^* = -\frac{(\mathbf{s}_i - \mathbf{s}_j) \cdot \mathbf{n}_i}{|\mathbf{s}_i - \mathbf{s}_j|^3}$$

For matrix \mathbf{D} ,

$$D_{ii} = D_{ii}^*$$

$$D_{ij} = D_{ji}^*$$

The finite element form of Eq. 24 becomes $\mathbf{T}\mathbf{q} = \mathbf{R}\phi^\rho$ with

$$\begin{aligned}\mathbf{T} &= \mathbf{S} - \frac{\epsilon - 1}{\epsilon + 1} \cdot \frac{1}{2\pi} \mathbf{SAD}^* \\ \mathbf{R} &= \frac{\epsilon - 1}{\epsilon + 1} \left[-1 + \frac{1}{2\pi} \mathbf{DA} \right].\end{aligned}$$

Chipman also suggested a symmetric form for \mathbf{T} as

$$\mathbf{T} = \mathbf{S} - \frac{\epsilon - 1}{\epsilon + 1} \cdot \frac{1}{4\pi} (\mathbf{DAS} + \mathbf{SAD}^*).$$

Appendix

The polarization density \mathbf{P} , for linear reponse material, is defined as[Wikipedia,GaussLaw]

$$\mathbf{P}(\mathbf{r}) = \chi_e \mathbf{E}(\mathbf{r}) \quad (27)$$

where χ_e is the electric susceptibility and \mathbf{E} is the local static electric field. The latter is defined as

$$\mathbf{E} = -\nabla\phi, \quad (28)$$

in which ϕ is the electrostatic potential. For discrete charges q_i distributed at \mathbf{r}_i ,

$$\phi(\mathbf{r}) = \sum_i \frac{q_i}{|\mathbf{r} - \mathbf{r}_i|}. \quad (29)$$

For continuous distribution of charges $\rho(\mathbf{r}_c)$,

$$\phi(\mathbf{r}) = \iiint_{\mathbf{V}} \frac{\rho(\mathbf{r}_c)}{|\mathbf{r} - \mathbf{r}_c|} d^3\mathbf{r}_c. \quad (30)$$

In Gaussian unit, $4\pi\epsilon_0 = 1$. The electric displacement field $\mathbf{D}(\mathbf{r})$ is

$$\begin{aligned}\mathbf{D} &= \mathbf{E} + 4\pi\mathbf{P} \\ &= (1 + 4\pi\chi_e)\mathbf{E} \\ &= \epsilon\mathbf{E}.\end{aligned} \quad (31)$$

The Gauss's law in the differential form reads

$$\nabla \cdot \mathbf{E} = 4\pi\rho, \quad (32)$$

and its integral form is

$$\oint\!\!\!\oint_{\mathbf{S}} \mathbf{E} \cdot d\mathbf{A} = 4\pi Q, \quad (33)$$

where Q is the total charge (not only the free charge Q_f , but also the polarized charge Q_p) in the volume enclosed by surface \mathbf{S} . The polarized (excess) charge is defined as

$$Q_p = - \oint\!\!\!\oint_{\mathbf{S}} \mathbf{P} \cdot d\mathbf{A}. \quad (34)$$

It can be easily found that

$$\begin{aligned} \oint\!\!\!\oint_{\mathbf{S}} \mathbf{D} \cdot d\mathbf{A} &= \oint\!\!\!\oint_{\mathbf{S}} (\mathbf{E} + 4\pi\mathbf{P}) \cdot d\mathbf{A} \\ &= 4\pi Q - 4\pi Q_p \\ &= 4\pi Q_f \end{aligned}$$

in the integral form. Alternatively, these two equations can be written in the differential form as

$$\nabla \cdot \mathbf{P} = -\rho_p, \quad (35)$$

$$\nabla \cdot \mathbf{D} = 4\pi\rho_f. \quad (36)$$

This equation shows that the electric displacement D is related to the free charge. Eq. 36 is also called the generalized Gauss's law. Utilizing the relation between \mathbf{D} and \mathbf{P} ,

$$\mathbf{D} = \epsilon\mathbf{E} = \frac{\epsilon}{\chi_e}\mathbf{P} = \frac{\epsilon}{\epsilon - 1}\mathbf{P} \quad (37)$$

we find

$$\rho_p = -\frac{\epsilon - 1}{\epsilon}\rho_f, \quad (38)$$

and

$$Q_p = -\frac{\epsilon - 1}{\epsilon}Q_f. \quad (39)$$

At the dielectric boundary between materials, the electric potential and the electric displacement are continuous, but not the electric field, i.e.

$$\phi_{\mathbf{S}^+} = \phi_{\mathbf{S}^-}, \quad (40)$$

and

$$\mathbf{D}_{\mathbf{S}^+} = \mathbf{D}_{\mathbf{S}^-}, \quad (41)$$

where \mathbf{S}^+ and \mathbf{S}^- are the outer and the inner surfaces, respectively. For electric field, we have

$$\epsilon_{\mathbf{S}^+} \cdot \mathbf{E}_{\mathbf{S}^+} = \epsilon_{\mathbf{S}^-} \cdot \mathbf{E}_{\mathbf{S}^-}, \quad (42)$$

which is a direct result from Eq. 41.

The divergence theorem

$$\iiint_V \nabla \cdot \mathbf{A} d^3\mathbf{r} = \oiint_{\Gamma} \mathbf{A} \cdot \mathbf{n}' d^2\mathbf{s}' \quad (43)$$

applies to any well-behaved vector field \mathbf{A} defined in the volume V bounded by the closed surface Γ . Let $\mathbf{A} = \phi \nabla(1/|\mathbf{r} - \mathbf{r}'|)$, where \mathbf{x} is the observation point and \mathbf{x}' is the integration variable to be used later. Now

$$\nabla \cdot (\phi \nabla(1/|\mathbf{r} - \mathbf{r}'|)) = \phi \nabla^2(1/|\mathbf{r} - \mathbf{r}'|) + \nabla \phi \cdot \nabla(1/|\mathbf{r} - \mathbf{r}'|) \quad (44)$$

and

$$\phi \nabla(1/|\mathbf{r} - \mathbf{s}'|) \cdot \mathbf{n}' = \phi \frac{\partial(1/|\mathbf{r} - \mathbf{s}'|)}{\partial \mathbf{n}'} \quad (45)$$

where $\partial/\partial n$ is the normal derivative at the surface Γ (directed outward from inside the volume V). Taking these two equations into the divergence theorem, we have the *Green's first identity*:

$$\iiint_V \left(\phi \nabla^2 \frac{1}{|\mathbf{r} - \mathbf{r}'|} + \nabla \phi \cdot \nabla \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right) d^3\mathbf{r} = \oiint_{\Gamma} \phi \frac{\partial}{\partial \mathbf{n}'} \frac{1}{|\mathbf{r} - \mathbf{s}'|} d^2\mathbf{s}'. \quad (46)$$

If we interchange ϕ and $\frac{1}{|\mathbf{r} - \mathbf{r}'|}$ in Eq. 46, we have

$$\iiint_V \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} \nabla^2 \phi + \nabla \frac{1}{|\mathbf{r} - \mathbf{r}'|} \cdot \nabla \phi \right) d^3\mathbf{r} = \oiint_{\Gamma} \frac{1}{|\mathbf{r} - \mathbf{s}'|} \frac{\partial \phi}{\partial \mathbf{n}'} d^2\mathbf{s}'. \quad (47)$$

Subtracting this equation from Eq. 46, we have *Green's second identity* or *Green's theorem*:

$$\iiint_V \left(\phi \nabla^2 \frac{1}{|\mathbf{r} - \mathbf{r}'|} - \frac{1}{|\mathbf{r} - \mathbf{r}'|} \nabla^2 \phi \right) d^3\mathbf{r} = \oint_{\Gamma} \left(\phi \frac{\partial}{\partial \mathbf{n}'} \frac{1}{|\mathbf{r} - \mathbf{s}'|} - \frac{1}{|\mathbf{r} - \mathbf{s}'|} \frac{\partial \phi}{\partial \mathbf{n}'} \right) d^2\mathbf{s}'. \quad (48)$$

We know that $\nabla^2 \frac{1}{|\mathbf{r} - \mathbf{r}'|} = -4\pi\delta(\mathbf{r} - \mathbf{r}')$ and $\nabla^2 \phi = -4\pi\rho$. Now we obtain

$$\iiint_V \left(-4\pi\phi(\mathbf{r}')\delta(\mathbf{r} - \mathbf{r}') + \frac{4\pi}{|\mathbf{r} - \mathbf{r}'|}\rho(\mathbf{r}') \right) d^3\mathbf{r} = \oint_{\Gamma} \left(\phi \frac{\partial}{\partial \mathbf{n}'} \frac{1}{|\mathbf{r} - \mathbf{s}'|} - \frac{1}{|\mathbf{r} - \mathbf{s}'|} \frac{\partial \phi}{\partial \mathbf{n}'} \right) d^2\mathbf{s}'. \quad (49)$$

If the point \mathbf{r} lies inside Γ , we obtain

$$\phi(\mathbf{r}) = \iiint_V \frac{1}{|\mathbf{r} - \mathbf{r}'|}\rho(\mathbf{r}')d^3\mathbf{r} + \frac{1}{4\pi} \oint_{\Gamma} \left(\frac{1}{|\mathbf{r} - \mathbf{s}'|} \frac{\partial \phi}{\partial \mathbf{n}'} - \phi \frac{\partial}{\partial \mathbf{n}'} \frac{1}{|\mathbf{r} - \mathbf{s}'|} \right) d^2\mathbf{s}'. \quad (50)$$

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