1 Ewald Sum (Allen)

The Ewald sum is a technique for efficiently summing the interaction between an ion and all its periodic images. It was originally developed in the study of ionic crystals [Madelung 1918]. The potential energy of a distribution of a set of charges z_j located in $\mathbf{r}_j$ in the simulated cell, can be written as

$$V = \frac{1}{2} \sum_{\mathbf{n}}' \sum_{i=1}^{N} \sum_{j=1}^{N} z_i z_j |\mathbf{r}_{ij} + \mathbf{n}|^{-1}$$

For simplicity of notation, we are omitting all factors of $4\pi\epsilon$: this corresponds to adopting a non-SI unit of charge. The sum over n is the sum over all simple cubic lattice points, $\mathbf{n} = (n_x L_x, n_y L_y, n_z L_z)$ with n_x, n_y and n_z integers. This vector reflects the shape of the basic box. The prime indicates that we omit $i = j$ for $n = 0$.

For long-range potentials, this sum is conditionally convergent, i.e. the result depends on the order in which we add up the terms. A natural choice is to take boxes in order of their proximity to the central box. The unit cells are added in sequence: the first term has $|\mathbf{n}| = 0$, i.e. $n = (0,0,0)$. The second term, $|\mathbf{n}| = 1$ comprises the six boxes centred at $n = (\pm 1, 0, 0)$, $n = (0, \pm 1, 0)$ and $n = (0, 0, \pm 1)$ etc. As we add further terms to the sum, we are building up our infinite system in roughly spherical layers. When we adopt this approach, we must specify the nature of the medium surrounding the sphere, in particular its relative permittivity (dielectric constant) ϵ. The results for a sphere surrounded by a good conductor such as a metal ($\epsilon = \infty$) and for a sphere surrounded by vacuum ($\epsilon = 1$) are different [de Leeuw, Perram, and Smith 1980].

$$V(\epsilon = \infty) = V(\epsilon = 1) - \frac{2\pi}{3L^2} |\sum_i z_i \mathbf{r}_i|^2 \tag{1}$$

This equation applies in the limit of a very large sphere of boxes. In the vacuum, the sphere has a dipolar layer on its surface: the last term in eqn 1 cancels this. For the sphere in a conductor there is no such layer. The Ewald method is a way of efficiently calculating $V(\epsilon = \infty)$. Equation 1 enables us

to use the Ewald sum in a simulation where the large sphere is in a vacuum, if this is more convenient.

1.1 Procedure

To calculate the potential energy, we first calculate the electrostatic potential in a generic point $\mathbf{r}_j$, e.g. the electrostatic potential experienced by one ion in the presence of all the other ions in the system. The basic idea is to evaluate the electrostatic potential in one point as a sum of two distinct related potentials. To this aim we consider the system as composed by the original charge distribution, plus two charge density distributions of gaussian shape, centered in the same position as the ions and with two opposite signs. In this way, the charge in the system is not altered. Both the charges and the two gaussians are copied in all periodic image cells. Finally, the two gaussians associated with the ion in $\mathbf{r}_j$ (as well as its charge z_j) are eliminated (but only in the central cell).

The electrostatic potential of this apparently more complicated system (the original charges and the sum of the two gaussian distributions) can be calculated as the sum of three pieces.

- The electrostatic potential ψ_a of a lattice with a Gaussian distribution of charge situated at each lattice point (in the infinite system), with signs the same as those of the real lattice.

- The electrostatic potential ψ_b of a single gaussian centered in $\mathbf{r}_j$ whose contribution needs to be subtracted

- The electrostatic potential ψ_c of a system composed by the ions and by their compensating Gaussian distribution with signs opposite to those of the ions.

The point of splitting the problem into parts is that by a suitable choice of the parameter determining the width of each Gaussian peak we can get very good convergence of both parts at the same time. The Gaussian distributions drop out completely on taking the sum of the separate charge distributions
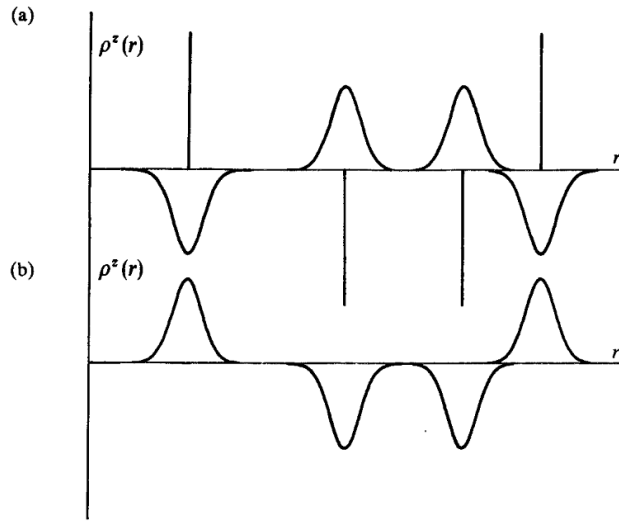
Fig. 5.8 Charge distribution in the Ewald sum. (a) Original point charges plus screening distribution. (b) Cancelling distribution.

Figure 1: Ewald method

giving rise to $\psi_a - \psi_b$, so that the value of the total potential ϕ is independent of the width parameter, but the rapidity of convergence depends on the value chosen for the parameter.

1.2 ψ_a

We calculate first the potential ψ_a of the periodic Gaussian distribution, composed of gaussians centered on the ions and on their periodic images (including ion j) e.g.

$$\rho(\mathbf{r}) = \sum_{\mathbf{n}} \sum_{i} z_i \left(\frac{\alpha}{\pi}\right)^{3/2} \exp[-\alpha|\mathbf{r_i} + \mathbf{n} - \mathbf{r}|^2]$$

We expand ψ_a and the charge density ρ in Fourier series:

$$\psi_a(\mathbf{r}) = \sum_{\mathbf{k}} c_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}}$$

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and

$$\rho(\mathbf{r}) = \sum_{\mathbf{k}} \rho_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} \tag{2}$$

These two quantities are related by the Poisson equation (just to remember... the Gauss theorem states that the flux of a vector is equal to the volume integral of the divergence of the same vector. Since the flux of the electric field is the volume integral of the charge density, it follows that the divergence of the electric field and hence the laplacian of the electric potential is equal to the charge density)

$$\nabla^2 \psi_a(\mathbf{r}) = -4\pi\rho(\mathbf{r})$$

which set a relation between $c_{\mathbf{k}}$ and $\rho_{\mathbf{k}}$. Indeed,

$$\sum_{\mathbf{k}} \left[-k^2 c_{\mathbf{k}} + 4\pi\rho_{\mathbf{k}} \right] e^{i\mathbf{k}\cdot\mathbf{r}} = 0$$
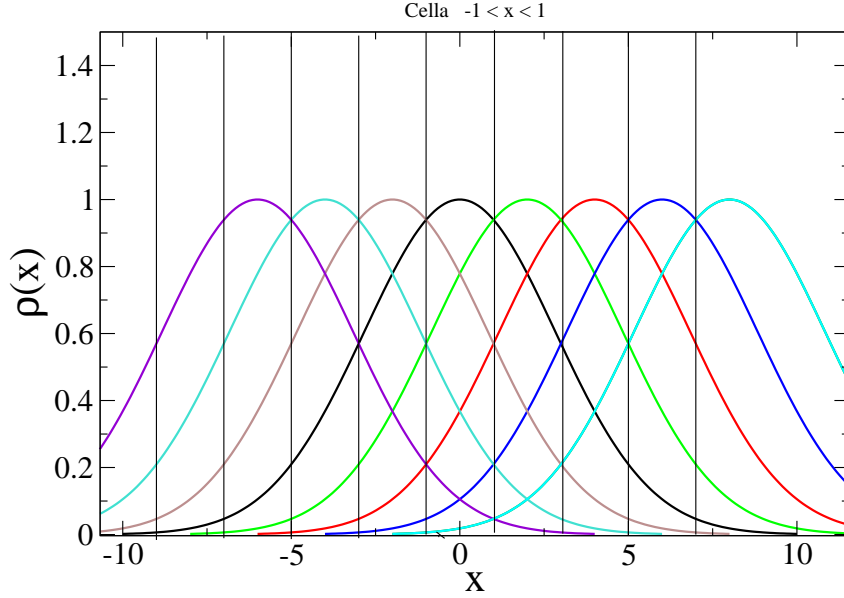
or

$$c_{\mathbf{k}} = \frac{4\pi}{k^2} \rho_{\mathbf{k}}$$

If we now multiply both sides of Eq. 2 by $e^{-i\mathbf{k}\cdot\mathbf{r}}$ and integrate over the cell volume

$$\int_V d\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}} \rho(\mathbf{r}) = \sum_{\mathbf{k}'} \rho_{\mathbf{k}'} \int_V d\mathbf{r} e^{i\mathbf{k}'\cdot\mathbf{r}} e^{-i\mathbf{k}\cdot\mathbf{r}} = \rho_{\mathbf{k}} V$$

$$\rho_{\mathbf{k}} = \frac{1}{V} \int_V d\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}} \rho(\mathbf{r})$$

Due to periodic boundary conditions, the integration over the cell volume can be transformed to an integration over the infinite volume of only the density originating in the central cell

Graphic demonstration that the integration over the original cell of $\rho(\mathbf{r})$ is equivalent to the integration of the gaussian in the original cell over all space

$$\rho(\mathbf{r}) = \sum_i z_i \left(\frac{\alpha}{\pi}\right)^{3/2} \exp[-\alpha|\mathbf{r_i} - \mathbf{r}|^2]$$

so that

$$\rho_{\mathbf{k}} = \frac{1}{V} \int d\mathbf{r} \sum_i e^{-i\mathbf{k}\cdot\mathbf{r}} \left(\frac{\alpha}{\pi}\right)^{3/2} \exp[-\alpha|\mathbf{r_i} - \mathbf{r}|^2]])$$

and

$$\psi_a(\mathbf{r}) = \sum_{\mathbf{k}} \frac{4\pi}{k^2} e^{i\mathbf{k}\cdot\mathbf{r}} \frac{1}{V} \int d\mathbf{t} \sum_i e^{-i\mathbf{k}\cdot\mathbf{t}} \left(\frac{\alpha}{\pi}\right)^{3/2} \exp[-\alpha|\mathbf{t} - \mathbf{r_i}|^2]])$$

Multiplying by $e^{-i\mathbf{k}\cdot\mathbf{r_i}} e^{+i\mathbf{k}\cdot\mathbf{r_i}}$ and completing the square [e.g. $-\{\frac{i\mathbf{k}}{2\sqrt{\alpha}}+\sqrt{\alpha}(\mathbf{t} - \mathbf{r_i})\}^2 = \frac{k^2}{4\alpha} - \alpha|\mathbf{t} - \mathbf{r_i}|^2 - i\mathbf{k}\cdot(\mathbf{t} - \mathbf{r_i})$] the integration over the normalized guassian gives one and

$$\psi_a(\mathbf{r}) = \sum_{\mathbf{k}} \frac{4\pi}{k^2} e^{i\mathbf{k}\cdot\mathbf{r}} \frac{1}{V} \sum_i z_i e^{-i\mathbf{k}\cdot\mathbf{r_i}} \exp\left[-\frac{k^2}{4\alpha}\right]$$

In $\mathbf{r}_j$, the point where the generic ion j is located

$$\psi_a(\mathbf{r}_j) = \frac{4\pi}{V} \sum_{\mathbf{k}} \frac{1}{k^2} \sum_i z_i e^{-i\mathbf{k}\cdot(\mathbf{r_i}-\mathbf{r_j})} \exp\left[-\frac{k^2}{4\alpha}\right]$$

Now summing over all ions in the simulation box, after multiplying for z_j to obtain the potential energy and dividing by two to avoid over counting,

$$V_a^{tot} = \frac{1}{2} \sum_j z_j \psi_a(\mathbf{r}_j) = \frac{1}{2} \sum_{j=1}^N \sum_{i=1}^N z_j z_i \frac{4\pi}{V} \sum_{\mathbf{k}} \frac{1}{k^2} e^{-i\mathbf{k}\cdot(\mathbf{r_i}-\mathbf{r_j})} \exp\left[-\frac{k^2}{4\alpha^2}\right]$$

1.3 ψ_b

Next we calculate the contribution in $\mathbf{r}_j$ of the electrostatic potential generated by the gaussian centered in $\mathbf{r}_j$. Indeed, in calculating ψ_a we have included also the gaussian in the central cell and now we need to correct for that. Locating $\mathbf{r}_j$ in the origin we are left with the calculation of the electrostatic potential at the origin due to a Gaussian distribution centered also in the origin. We can calculated this electrostatic potential making use of Gauss theorem to evaluate the electric field of a spherical charge distribution

$$\psi_b(\mathbf{r}=0) = -\int_\infty^0 E(R)dR = -\int_\infty^0 \frac{\int_0^R d\mathbf{t}\rho(t)}{R^2}dR = \int_0^\infty \int_0^R d\mathbf{t}\rho(t)\frac{1}{R^2}dR$$

By changing the integration limits to $0 < t < \infty$ and $t < R < \infty$,

$$\psi_b(\mathbf{r}=0) = -\int_0^\infty \rho(t)4\pi t^2 dt \int_t^\infty \frac{1}{R^2}dR = 4\pi \int_0^\infty \rho(t)tdt$$

For the Gaussian distribution, changing tdt in $d(\alpha t^2)/2\alpha$, one gets

$$\psi_b(\mathbf{r}=0) = 4\pi \left(\frac{\alpha}{\pi}\right)^{3/2} \frac{1}{2\alpha} = 2\left(\frac{\alpha}{\pi}\right)^{1/2}$$

If the Gaussian models an ion of valence z_i, this value need to be multiplied by z_i

When summing over all ions in the system, after multiplying again by z_i to obtain the potential energy, we get a contribution

$$V_b^{tot} = 2 \sum_i z_i^2 \left(\frac{\alpha}{\pi}\right)^{1/2}$$

1.4 ψ_c

The electrostatic potential ψ_c is the potential generated by all charges in the system associated to a gaussian distribution with opposite sign whose center il located on the same charge.

The appendix shows how to calculate the potential $V(R)$ generated by a gaussian distribution at distance R from its center,

$$V(R) = \frac{1}{R} - \frac{Erfc(\sqrt{\alpha}R)}{R}$$

Adding the contribution of the charge on the same location eliminates the $1/R$ term, leaving only $Erfc(\sqrt{\alpha}R)$.

Focusing on the electrostatic potential created in $\mathbf{r}_i$ by all other ions in the system one get

$$\psi_c^{tot}(\mathbf{r}_j) = \sum_{\mathbf{n}} \sum_{i=1,i\neq j}^{N} z_i \frac{Erfc(\sqrt{\alpha}|\mathbf{r}_i + \mathbf{n} - \mathbf{r}_j|)}{|\mathbf{r}_i + \mathbf{n} - \mathbf{r}_j|}$$

Now summing over all ions in the simulation box, after multiplying for z_j to obtain the potential energy and dividing by two to avoid over counting

$$V_c^{tot} = \frac{1}{2} \sum_j z_j \psi_2^{tot,j}(\mathbf{r}_j) = \frac{1}{2} \sum_{\mathbf{n}}' \sum_{j=1}^{N} \sum_{i=1}^{N} z_j z_i \frac{Erfc(\sqrt{\alpha}|\mathbf{r}_i + \mathbf{n} - \mathbf{r}_j|)}{|\mathbf{r}_i + \mathbf{n} - \mathbf{r}_j|}$$

(as before the prime indicates that we omit $i = j$ for $n = 0$).

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2   Result

The final potential energy thus contains a real space sum plus a reciprocal space sum minus a self-term plus the surface term already discussed. The final result is

$$V(\epsilon = 1) = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \left(\sideset{}{'}\sum_{\mathbf{n}} z_i z_j \frac{erfc(\kappa|\mathbf{r}_{ij} + \mathbf{n}|)}{|\mathbf{r}_{ij} + \mathbf{n}|} + \frac{1}{\pi L^3} \sum_{\mathbf{k} \neq 0} z_i z_j \frac{4\pi^2}{k^2} e^{-k^2/4\kappa^2} cos(\mathbf{k} \cdot \mathbf{r}_{ij}) \right)$$

$$- \frac{\kappa}{\pi^{1/2}} \sum_{i=1}^{N} z_i^2 + \frac{2\pi}{3L^2} |\sum_{i=1}^{N} z_i \mathbf{r}_i|^2 \qquad (3)$$

Here $erfc(x)$ is the complementary error function ($erfc(x) = (2/\pi^{1/2}) \int_x^\infty e^{-t^2} dt$) which falls to zero with increasing x. Thus, if κ is chosen to be large enough, the only term which contributes to the sum in real space is that with n = 0, and so the first term reduces to the normal minimum image convention. The second term is a sum over reciprocal vectors $\mathbf{k} = \frac{2\pi}{L}\mathbf{n}$. A large value of κ corresponds to a sharp distribution of charge, so that we need to include many terms in the k-space summation to model it. In a simulation, the aim is to choose a value of κ and a sufficient number of k-vectors, so that Eqn 3 (with the real space sum truncated at n = 0) and the total sum give the same energy for typical liquid configurations. In practice, κ is typically set to 5/L and 100-200 wave vectors are used in the k-space sum [Woodcock and Singer 1971]. We stress that checks should be carried out on the reliability of Eqn 3 for each individual system which is simulated before beginning the run.

The original method of Ewald can be readily extended to dipolar systems. In the derivation of eqn (5.20), z_i is simply replaced by $\vec{\mu}_i \cdot \nabla_{\mathbf{r}_i}$ where $\vec{\mu}_i$ is the particle dipole. The resulting expression is [Kornfeld 1924; Adams and McDonald 1976; de Leeuw et al. 1980.]

$$V^\mu(\epsilon = 1) =$$

$$\frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\left(\sum_{|\mathbf{n}|=0}^{\infty'}(\mu_i\cdot\mu_j)B(|\mathbf{r}_{ij}+\mathbf{n}|)-(\mu_i\cdot\mathbf{r}_{ij})(\mu_j\cdot\mathbf{r}_{ij})C(|\mathbf{r}_{ij}+\mathbf{n}|)+\sum_{\mathbf{k}\neq0}\frac{1}{\pi L^3}(\mu_i\cdot\mathbf{k})(\mu_j\cdot\right.$$

$$-\frac{2\kappa^3\mu_i^2}{3\sqrt{\pi}}+\frac{1}{2}\sum_{i=1}^{N}|\sum_{j=1}^{N}\frac{4\pi}{3L^3}\mu_i\cdot\mu_j \tag{4}$$

where

$$B(r)=erfc(\kappa r)/r^3+\frac{2\kappa}{\sqrt{\pi}}e^{-k^2r^2}/r^2$$

and

$$C(r)=3erfc(\kappa r)/r^5+\frac{2\kappa}{\sqrt{\pi}}(2\kappa^2+3/r^2)e^{-k^2r^2}/r^2$$

This expression can be used in the same way as the Ewald sum, with the real space sum truncated at $|\mathbf{n}|=0$ and a separate subroutine to calculate the k-vector sum. Smith [1982a] has given an elegant formulation of the extension of the Ewald method to dipoles and quadrupoles; his article contains explicit expressions for forces and torques which will be of use in MD simulations.

3   reaction field (Allen)

In the reaction field method, the field on a dipole in the simulation consists of two parts: the first is a short-range contribution from molecules situated within a cutoff sphere or 'cavity' $\mathcal{R}$, and the second arises from molecules outside $\mathcal{R}$ which are considered to form a dielectric continuum (ϵ_s) producing a reaction field within the cavity [Onsager 1936]. The size of the reaction field $\mathbf{E}_i$ acting on molecule i is proportional to the moment of the cavity surrounding i

$$\mathbf{E}_i=\frac{2(\epsilon_s-1)}{2\epsilon_s+1}\frac{1}{r_c^3}\sum_{j\in\mathcal{R}}\mu_j$$

where the summation extends over the molecules in the cavity, including i, and r_c is the radius of the cavity. The contribution to the energy from the reaction field is $-\frac{1}{2}\mu_i\cdot\mathbf{E}_i$. The torque on molecule i from the reaction

field is $\mu_i \times \mathbf{E}_i$ Barker and Watts [1973] first used the reaction field in a simulation of water, and there are useful discussions by Friedman [1975] and Barker [1980]. Whenever a molecule enters or leaves the cavity surrounding another, a discontinuous jump occurs in the energy due to direct interactions within the cavity and in the reaction field contribution. These changes do not exactly cancel, and the result is poor energy conservation in MD. In addition, spurious features appear in the radial distribution function at $r = r_c$ These problems may be avoided by tapering the interactions at the cavity surface [Adams, Adams, and Hills 1979]: the explicit interactions between molecules i and j are weighted by a factor $f(r_{ij})$, which approaches zero continuously at $r_{ij} = r_c$.

The static reaction field is straightforward to calculate in a conventional MD or MC simulation, and it involves only a modest increase in execution time. A potential difficulty with the reaction field method is the need for an a priori knowledge of the external dielectric constant ϵ_s. Fortunately, the thermodynamic properties of a dipolar fluid are reasonably insensitive to the 'choice of ϵ_s.

3.1 Appendix A

Here we calculate the electrostatic potential generated by a spherical charge distribution in a point at distance R from its center.

According to the Gauss theorem, in a generic point at distance r from the center of the spherical distribution $\rho(\mathbf{r})$, the electric field is

$$E(r) = \frac{\int_0^r \rho(t) 4\pi t^2 dt}{r^2}.$$

The electrostatic potential at distance R can be calculated integrating the electric field from infinite to R

$$\phi(R) = -\int_\infty^R E(r) dr$$

so that

$$\phi(R) = -\int_\infty^R dr \int_0^r dt \frac{1}{r^2}\rho(t)4\pi t^2$$

By changing the integration limits from

$$R < r < \infty$$
$$0 < t < r \tag{5}$$

to (splitting $0 < t < r$ in two parts $0 < t < R$ and $R < t < r$)

$$0 < t < R$$
$$R < r < \infty \tag{6}$$

and

$$R < t < \infty$$
$$t < r < \infty \tag{7}$$

one gets

$$\phi(R) = -\int_R^\infty dt\rho(t)4\pi t^2 \int_t^\infty \frac{dr}{r^2} - \int_0^R dt\rho(t)4\pi t^2 \int_R^\infty \frac{dr}{r^2} =$$

$$\phi(R) = \int_R^\infty dt\rho(t)4\pi t^2 \frac{1}{t} + \int_0^R dt\rho(t)4\pi t^2 \frac{1}{R} = \int_R^\infty d\mathbf{t}\frac{\rho(t)}{t} + \frac{1}{R}\int_0^R d\mathbf{t}\rho(t)$$

which can also be written as

$$\phi(R) = \int_R^\infty d\mathbf{t}\frac{\rho(t)}{t} + \frac{1}{R}\left[\int_0^R d\mathbf{t}\rho(t) + \int_R^\infty d\mathbf{t}\rho(t) - \int_R^\infty d\mathbf{t}\rho(t)\right] =$$
$$\int_R^\infty d\mathbf{t}\frac{\rho(t)}{t} + \frac{1}{R} - \frac{1}{R}\int_R^\infty d\mathbf{t}\rho(t)$$

When (assuming an integrated unit charge)

$$\rho(r) = \left(\frac{\alpha}{\pi}\right)^{3/2} \exp[-\alpha r^2]$$

$$\phi(R) = \frac{1}{R} + 4\pi \left(\frac{\alpha}{\pi}\right)^{3/2} \left(\int_R^\infty dr\, r \exp[-\alpha r^2] - \frac{1}{R} \int_R^\infty dr\, r^2 \exp[-\alpha r^2]\right)$$

Considering that $dr\, r \exp[-\alpha r^2] = -d\exp[-\alpha r^2]/(2\alpha)$ and that $dr\, r^2 \exp[-\alpha r^2] = -r d\exp[-\alpha r^2]/(2\alpha)$ we get (integrating by part the second integral)

$$\phi(R) = \frac{1}{R} + 4\pi \left(\frac{\alpha}{\pi}\right)^{3/2} \left(\frac{\exp[-\alpha R^2]}{2\alpha} - \frac{1}{R}\left[\frac{R\exp[-\alpha R^2]}{2\alpha} - \int_R^\infty \frac{\exp[-\alpha r^2]}{2\alpha} dr\right]\right) =$$

$$\phi(R) = \frac{1}{R} - 4\pi \left(\frac{\alpha}{\pi}\right)^{3/2} \frac{1}{R} \int_R^\infty \exp[-\alpha r^2]/(2\alpha) dr = \frac{1}{R} - 2\left(\frac{\alpha}{\pi}\right)^{1/2} \frac{1}{R} \int_R^\infty \exp[-\alpha r^2] dr =$$

$$= \frac{1}{R} - \frac{1}{R}\frac{2}{\sqrt{\pi}} \int_{\sqrt{\alpha}R}^\infty \exp[-t^2] dt = \frac{1}{R} - \frac{1}{R} Erfc(\sqrt{\alpha}R)$$

where we have defined the complementary error function

$$erfc(x) = \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-x^2} dx$$