Modelling the interaction of nanotube with particles of the medium by the Green's function method

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Abstract. The end surface of a cylindrical nanotube is considered as an annular and is replaced by a torus by solving the electrostatic problems, they are 1) the interaction of a charged particle with a torus and 2) the interaction of a charged torus with a neutral particle. Solution of the Poisson equation is given in the toroidal coordinate system and expressed by a half-order Legendre function of the first and second kind. The convergence of series expansion is improved by a given transformation of corresponding hypergeometric functions. The calculations are represented for the axially symmetric case.

In recent years interest in such nanostructures in which the particle, or fullerene molecule with a great polarizability is situated inside a carbon nanotube is sharply increased. These objects can be widely used in microelectronics, optics and biophysics. Materials based on them are promising nanocomposites [1-2]. Also annular and coiled nanostructure are of special interest [3].

An approach and a retraction of a particle to a nanotube is mainly due to non-covalent interactions having a classical electrostatic nature.

The open end of a nanotube is a ring of finite thickness and it is approximated by a torus of radius \( a \) by the solution of electrostatic problems. The toroidal coordinates \((\eta, \theta, \varphi)\) are expressed through the Cartesian by

\[
x = a \frac{\sinh \eta \cos \varphi}{\cosh \eta - \cos \theta}, \quad y = a \frac{\sinh \eta \sin \varphi}{\cosh \eta - \cos \theta}, \quad z = a \frac{\sin \theta}{\cosh \eta - \cos \theta}
\]

and are used by the solution of the Poisson's equation in terms of a Green function. Radius \( a \), a scale parameter of torus, is

\[
a = \sqrt{R_0^2 - R_t^2},
\]

where \( R_0 \) is an exterior radius, or in our case it is a radius of a nanotube, \( R_t \) is a thickness of torus. Thickness is considered to be equal to the van der Waals radius of carbon, 0.17 nm [4].

The essence of the method used for solving such problems is to find the Green's function which satisfies Poisson's equation in chosen coordinate system

\[
\Delta G(r, r_0) = -4 \pi \varepsilon \delta(r - r_0),
\]

where \( r_0 \) is radius vector of a point charge, \( \delta(r - r_0) \) is Dirac delta function and \( \varepsilon \) is dielectric permittivity, and the boundary conditions at the surface, in this case on the toroidal surface.

\[
G(r, r_0)|_{\partial S} = 0
\]

Firstly, the problem of a point unit charge above the torus is considered. Green's function consists of two components – the Coloumb potential part \( G(r, r_0) \) of a point charge in an unbounded region.
Hypergeometric series which expresses the Legendre function of the second kind is conveniently
accommodate a large number of terms in the partial sum.

Applying this transformation to (10) is easy to obtain

\[ G_0(r, r_0) = G_0(r, r_0) + R(r, r_0) \]

Thus we get series in powers of the hyperbolic tangent, which converges quickly enough.

After the separation of variables in the equation (2), see for instance [4], the expression for the
Coulomb potential can be written as

\[ G_0(r, r_0) = -\frac{q}{4\pi\varepsilon a} \sqrt{(\cosh \eta - \cos \theta)(\cosh \eta - \cos \theta_0)} \sum_{n=0}^{\infty} \xi_n \cos n(\theta - \theta_0) \times \]

\[ \times (-1)^m \frac{\Gamma(n-m+1/2)}{\Gamma(n+m+1/2)} \left[ P_{n-1/2}^m(\cosh \eta)P_{n-1/2}^m(\cosh \eta) + P_{n-1/2}^m(\cosh \eta)Q_{n-1/2}^m(\cosh \eta)Q_{n-1/2}^m(\cosh \eta) \right] \]

where \( \xi_n \) takes value 1 for \( n, m = 0 \) and 2 for \( n, m > 0 \), \( P_{n-1/2}^m \) and \( Q_{n-1/2}^m \) are associated Legendre functions of first and second kind respectively, \( \Theta(\eta - \eta_0) \) is a unit step function, \( q \) is a unit charge. The
expression for the reactive fields takes correspondingly the form

\[ R(r, r_0) = -\frac{q}{4\pi\varepsilon a} \sqrt{(\cosh \eta - \cos \theta)(\cosh \eta - \cos \theta_0)} \sum_{n=0}^{\infty} \xi_n \sin n(\theta - \theta_0) \times \]

\[ \times (-1)^m \frac{\Gamma(n-m+1/2)}{\Gamma(n+m+1/2)} P_{n-1/2}^m(\cosh \eta)Q_{n-1/2}^m(\cosh \eta) [Q_{n-1/2}^m(\cosh \eta)]^2 \]

The resulting formulas are considerably simplified in the axially symmetric case, when the charge
is located on the axis \( z \) and accordingly \( \eta_0 = 0 \), then the dependence of angle \( \phi \) disappears and we obtain

\[ G_0(r, r_0) = -\frac{q}{4\pi\varepsilon a} \sqrt{(\cosh \eta - \cos \theta)(1-\cos \theta_0)} \sum_{n=0}^{\infty} \xi_n \cos n(\theta - \theta_0) Q_{n-1/2}^m(\cosh \eta) \]

\[ R(r, r_0) = -\frac{q}{4\pi\varepsilon a} \sqrt{(\cosh \eta - \cos \theta)(1-\cos \theta_0)} \sum_{n=0}^{\infty} \xi_n \sin n(\theta - \theta_0) Q_{n-1/2}^m(\cosh \eta) \]

\[ \times (-1)^m \frac{\Gamma(n-m+1/2)}{\Gamma(n+m+1/2)} P_{n-1/2}^m(\cosh \eta)Q_{n-1/2}^m(\cosh \eta) \]

\[ P_{n-1/2}(\cosh \eta) = -2F_1\left(\frac{1}{2} - n, \frac{1}{2} + n; 1; \frac{1 - \cosh \eta}{2}\right) \]

\[ Q_{n-1/2}(\cosh \eta) = (\Gamma(n + \frac{1}{2})/\Gamma(n + 1))(2 \cosh \eta)^{n-1/2} \times 2F_1\left(\frac{n}{2}, \frac{3}{4}; \frac{3}{2}; \frac{n + 1}{2}; \cosh^{-2} \eta\right) \]

However, for practical purposes, these expressions for the function of the first kind and the functions
of the second kind are inconvenient due to the slow convergence hypergeometric series and need
accommodate a large number of terms in the partial sum.

To improve the convergence of the hypergeometric function transform using known relationships
by Kummer. In the case of functions of the first kind of the optimal transformation is done as follows:

\[ _2F_1(a, b; c; z) = (1 - z)^{-a} _2F_1\left(a, b - c; \frac{1 - z}{1 - \frac{1}{z}}\right) \]

Applying this transformation to (10) is easy to obtain

\[ P_{n-1/2}(\cosh \eta) = \left(\frac{\cosh \eta + 1}{2}\right)^{n-1/2} _2F_1\left(\frac{1}{2} - n, \frac{1}{2} - n - 1; - \tanh^2 \frac{\eta}{2}\right) \]

Thus we get series in powers of the hyperbolic tangent, which converges quickly enough. Hypergeometric series which expresses the Legendre function of the second kind is conveniently
subjected to the following sequence of transformations: first, to make the quadratic transformation:

\[ _2F_1\left(a, a + \frac{1}{2}; c; z\right) = (1 - z)^{-a} _2F_1\left(2a, 2c - 2a - 1; c; \frac{1}{2} \left(1 - \frac{1}{1 - \frac{1}{z}}\right)\right) \]

and then use the transform (12). The result is the following rapidly converging series in powers of exponent:
Thus the series obtained using (13) and (15) can be used for further quantitative assessment of the effect. Table 1 shows a comparison of values of Legendre functions with an integer index, which can be calculated with high accuracy, given in [7] and obtained by the proposed method. Table 2 shows a comparison of Legendre functions with half-integer index calculated through elliptic integrals and the proposed method.

Table 1. Comparison of Legendre functions values with integer index \( n = 0(1)4 \) obtained in [7] and by the proposed method.

| \( n \) | \( P_n(z) \), \( z = 2.6000 \) | \( Q_n(z) \), \( z = 2.6000 \) |
|---|---|---|
| 0 | 1.0000 | 1.0000 |
| 1 | 2.6000 | 2.6001 |
| 2 | 9.6400 | 9.6400 |
| 3 | 40.0400 | 40.0395 |
| 4 | 174.9520 | 174.9500 |

Table 2. Comparison of Legendre functions values with half-integer index \( n = \pm \frac{1}{2} \) obtained by using full elliptic integral representation [7] and by the proposed method.

| \( n \) | \( P_{n+1/2}(z) \), \( z = 8.8235 \) | \( Q_{n+1/2}(z) \), \( z = 8.8235 \) |
|---|---|---|
| \(-\frac{1}{2}\) | 0.6461 | 0.6420 |
| \( \frac{1}{2} \) | 2.6862 | 2.6864 |

Polarization energy in the case of the set of point charges consists of summ of single-particle contributions \( U_i \) and two-particle contributions \( U_{ij} \) which are due to the interaction of charge \( q_i \) with the reactive field of \( q_j \).

\[
P_i = \frac{q_i}{2} \int \delta(r - r_i) R(r, r_i) d^3r, \qquad U_{ij} = \frac{q_i q_j}{2} \int d^3r' \int \delta(r' - r_i) R(r, r') \delta(r - r_j) d^3r
\]  

(16)

Polarization energy of unit point charge is given by the first term in (16). After substitution (9) with the assumption that the charge is on the \( z \)-axis in (16) and simplifying we get

\[
U = -\frac{a \Lambda(s)}{4 \pi \varepsilon} \frac{q^2}{a^2 + z_0^2},
\]  

(17)

where by \( \Lambda(s) \) denotes the series, which, as can be shown by using the asymptotic formulas for the Legendre functions converges uniformly:

\[
\Lambda(s) = \sum_{n=0}^{\infty} \xi_n \left( \frac{Q_{n-1/2}(\cosh s)}{P_{n-1/2}(\cosh s)} \right)
\]  

(18)

Values of constant \( \Lambda(s) \) calculated for different radii \( R_0 \) of nanotube and respectively for different \( s \) are given in table 3

Table 3. Values of \( \Lambda(s) \).

| \( R_0, \text{nm} \) | \( \text{cosh } s \) | \( \Lambda(s) \) |
|---|---|---|
| 1.0 | 5.8824 | 1.3332 |
| 1.5 | 8.8235 | 1.1837 |
| 2.0 | 11.7647 | 1.1100 |
| 5.0 | 29.4118 | 1.1079 |

Force component acting upon a unit charge can be calculated as a derivative of the reactive field

\[
F_\theta = -q \frac{1}{H_0} \frac{\partial R}{\partial \theta} \bigg|_{r=r_0},
\]  

(19)
where $H_0$ is a Lame coefficient which is equal to $a/(\cosh \eta - \cos \theta)$. Also force can be calculated by the gradient energy. Of course, both approaches should give the same result. So component of the force acting in the $z$ direction is given by

$$F_z = \frac{q^2 a \Lambda(s)}{2 \pi^2 \varepsilon} \frac{z_0}{(a^2 + z_0^2)^2}.$$  \hspace{1cm} (20)\]

In the axial symmetric case the computation of force, acting the charge, and polarization energy was done. Thickness of torus is considered to be 0.17 nm as was told earlier, radius of nanotube is changed. Plots for calculated force (figure 1) and energy (figure 2) are given for the case of unit point charge located on $z$-axis.

**Figure 1.** Force $F$, N/mol acting upon a unit point charge as functions of distance $z_0$, nm to the centre of ring.

**Figure 2.** Polarization energy $U$, kJ/mol as functions of distance $z_0$, nm to the centre of ring of ring.

Summing up, solution of the Poisson's equation was presented in the toroidal coordinate system and expressed by a half-order Legendre function of the first and second kind. Transformation of hypergeometric functions was done. Numerical calculations, plots of energy and force were represented for the axially symmetric case.

**References**

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