Lennard-Jones Potential inside a Spherical Cavity

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Abstract

The Lennard-Jones potential for an atom inside a conducting spherical cavity is derived. The interest is in possible anomalous effects near the focal point of a cavity viewed as a spherical mirror. We find a smooth dependence of the potential on the distance of the atom from the surface of the cavity.

1 Plane Mirror and the C_3 coefficient

Let us consider first a plane mirror, assumed to lie in the $x-y$ plane. We locate a nucleus of charge Z at a distance L on the z axis above the plane. We suppose that there are Z electrons located at coordinates $\vec{\rho_i} = (\xi_i,\, \eta_i,\, \zeta_i)$ relative to the nucleus. The image of the nucleus is at the point $(0,\, 0,\, -L)$ and the images of the electrons are located at points $(\xi_i,\, \eta_i,\, -L-\zeta_i)$.

Assuming that the mirror is grounded, $\Phi(x,y,0)=0$, the potential at any point can be written as $\Phi(x,y,z) = \Phi_0(x,y,z) + \Phi_I(x,y,z)$, where Φ_0 is the potential of the charges in the absence of the mirror and Φ_I is the potential of the image charges introduced to maintain the mirror potential at ground. We have

$$\Phi_I(x,y,z) = -\frac{Z|e|}{4\pi\epsilon_0}\,\frac{1}{\sqrt{x^2+y^2+(z+L)^2}} + \sum_i \frac{|e|}{4\pi\epsilon_0}\,\frac{1}{\sqrt{(x-\xi_i)^2+(y-\eta_i)^2+(z+L+\zeta_i)^2}}. \qquad (1)$$

The potential energy

$$U = \frac{1}{2}\sum_k q_k \Phi(\vec{r}_k) \qquad (2)$$

breaks up into two parts $U = U_0 + U_I$; the first U_0 is the (uninteresting) energy of the atom in absence of mirror and the second U_I is the energy of interaction of the atom and its image. We may write

$$U_I = Z|e|\,\Phi_I(0,0,L) - \sum_j |e|\,\Phi_I(\xi_j,\,\eta_j,\,L+\zeta_j). \tag{3}$$

This expression may be rewritten as

$$\begin{aligned} U_I &= -\frac{Z^2e^2}{4\pi\epsilon_0}\frac{1}{2L} \\ &+ \frac{Ze^2}{4\pi\epsilon_0}\sum_i \frac{1}{\sqrt{\xi_i^2+\eta_i^2+(2L+\zeta_i)^2}} \\ &+ \frac{Ze^2}{4\pi\epsilon_0}\sum_j \frac{1}{\sqrt{\xi_j^2+\eta_j^2+(2L+\zeta_j)^2}} \\ &- \frac{e^2}{4\pi\epsilon_0}\sum_{ij} \frac{1}{\sqrt{(\xi_i-\xi_j)^2+(\eta_i-\eta_j)^2+(2L+\zeta_j+\zeta_j)^2}} \end{aligned} \tag{4}$$

The following 2nd-order expansion formulas are useful:

$$\frac{1}{\sqrt{\xi_i^2+\eta_i^2+(2L+\zeta_i)^2}} = \frac{1}{2L}\left[1-\frac{\zeta_i}{2L}+\frac{3\zeta_i^2-\rho_i^2}{8L^2}\right] \tag{5}$$

and

$$\begin{aligned} &\frac{1}{\sqrt{(\xi_i-\xi_j)^2+(\eta_i-\eta_j)^2+(2L+\zeta_j+\zeta_j)^2}} \\ &\quad= \frac{1}{2L}\left[1-\frac{\zeta_i+\zeta_j}{2L}+\frac{3\zeta_i^2+3\zeta_j^3-\rho_i^2-\rho_j^2}{8L^2}+\frac{\xi_i\xi_j+\eta_i\eta_j+2\zeta_i\zeta_j}{4L^2}\right], \end{aligned} \tag{6}$$

where $\rho_i^2 = \xi_i^2+\eta_i^2+\zeta_i^2$. Substituting into Eq. (4) from Eqs. (5) and (6), one finds that all terms of 0th and 1st order in atomic dimensions cancel leaving as a remainder

$$U_I = -\frac{e^2}{8\pi\epsilon_0}\,\frac{1}{8L^3}\sum_{ij}\left(\xi_i\xi_j+\eta_i\eta_j+2\zeta_i\zeta_j\right). \tag{7}$$

For a spherically symmetric atom one can average the double sum over electronic coordinates to find

$$\left\langle \sum_{ij}\left(\xi_i\xi_j+\eta_i\eta_j+2\zeta_i\zeta_j\right)\right\rangle = \frac{4}{3}\left\langle \sum_{ij}\vec{\rho}_i\cdot\vec{\rho}_j\right\rangle = \frac{4}{3}\left\langle R_{\rm atom}^2\right\rangle, \tag{8}$$

where $R_{\rm atom}$ is the atomic radius. One finally obtains the well-known Lennard-Jones [1] result for the atom-surface interaction:

$$\langle U_I\rangle = -\frac{e^2}{4\pi\epsilon_0}\,\frac{C_3}{L^3}, \tag{9}$$

with

$$C_3 = \frac{1}{12}\langle R_{\rm atom}^2\rangle. \tag{10}$$

2 Spherical Images

Now, let us consider a conducting sphere of radius a and imagine an atom with nuclear charge Z located at the point $R < a$, which we choose for convenience to be on the z axis, $\vec{R} = R\hat{z}$. The bound electrons are assumed to be located at positions $\vec{r}_i = \vec{R} + \vec{\rho}_i$. The image of the nucleus is located at a distance

$$d = \frac{a^2}{R}$$

from the origin on the z axis. Similarly, the images of the electrons are at distances

$$d_i = \frac{a^2}{r_i}$$

from the origin and have the same polar angles θ_i and ϕ_i as the respective real charges.

The image potential can be written:

$$\begin{aligned} \Phi_I(\vec{r}) = &-\frac{Z|e|}{4\pi\epsilon_0} \frac{a}{\sqrt{a^4 - 2a^2\vec{r}\cdot\vec{R} + R^2r^2}} \\ &+ \sum_i \frac{|e|}{4\pi\epsilon_0} \frac{a}{\sqrt{a^4 - 2a^2\vec{r}\cdot\vec{r}_i + r_i^2r^2}} \end{aligned} \tag{11}$$

The interaction energy is again given by Eq. (2) leading to

$$\begin{aligned} U_I &= -\frac{Z^2e^2}{8\pi\epsilon_0}\frac{a}{a^2 - R^2} \\ &+ \frac{Ze^2}{8\pi\epsilon_0}\sum_i \frac{a}{\sqrt{a^4 - 2a^2\vec{R}\cdot\vec{r}_i + r_i^2R^2}} \\ &+ \frac{Ze^2}{8\pi\epsilon_0}\sum_j \frac{a}{\sqrt{a^4 - 2a^2\vec{R}\cdot\vec{r}_j + r_j^2R^2}} \\ &- \frac{e^2}{8\pi\epsilon_0}\sum_{ij} \frac{a}{\sqrt{a^4 - 2a^2\vec{r}_i\cdot\vec{r}_j + r_i^2r_j^2}}. \end{aligned} \tag{12}$$

We use the expansions

$$\frac{a}{\sqrt{a^4 - 2a^2\vec{R}\cdot\vec{r}_i + r_i^2R^2}} = \frac{a}{a^2 - R^2}\left[1 + \frac{\vec{R}\cdot\vec{\rho}_i}{a^2 - R^2} + \frac{3(\vec{R}\cdot\vec{\rho}_i)^2 - R^2\rho_i^2}{2(a^2 - R^2)^2}\right], \tag{13}$$

and

$$\frac{a}{\sqrt{a^4 - 2a^2\vec{r}_i\cdot\vec{r}_j + r_i^2r_j^2}} = \frac{a}{a^2 - R^2}\left[1 + \frac{\vec{R}\cdot\vec{\rho}_i + \vec{R}\cdot\vec{\rho}_j}{a^2 - R^2}\right.$$

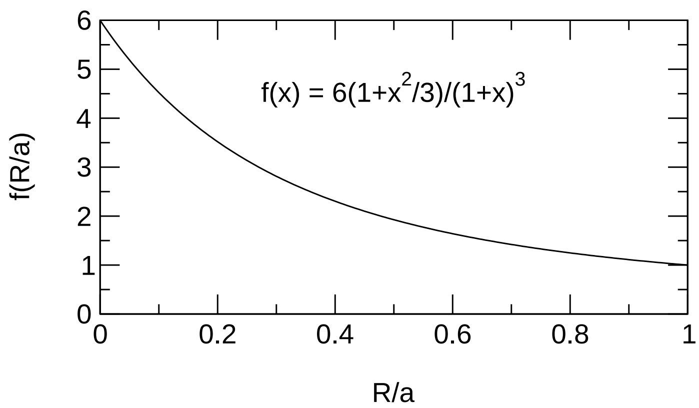

Figure 1: The function $f(R/a)$ for a conducting spherical cavity.

$$+\frac{3(\vec{R}\cdot\vec{\rho}_i)^2+3(\vec{R}\cdot\vec{\rho}_j)^2-R^2\rho_i^2-R^2\rho_j^2}{2(a^2-R^2)^2}$$
$$\left.+\frac{a^2\vec{\rho}_i\cdot\vec{\rho}_j+(\vec{R}\cdot\vec{\rho}_i)(\vec{R}\cdot\vec{\rho}_j)}{(a^2-R^2)^2}\right] . \tag{14}$$

Expanding the terms in Eq. (12), one can easily verify that the terms of 0th and 1st order in the electron-nucleus separation vanish. The residual second-order terms give

$$U_I = -\frac{e^2}{8\pi\epsilon_0}\frac{a^3}{(a^2-R^2)^3}\sum_{ij}\left(\vec{\rho}_i\cdot\vec{\rho}_j+\frac{R^2}{a^2}\,\zeta_i\zeta_j\right) . \tag{15}$$

Assuming spherical symmetry for the atom and averaging over electron coordinates, one can rewrite this as

$$\langle U_I\rangle = -\frac{e^2}{4\pi\epsilon_0}\frac{C_3}{(a-R)^3}\; f(R/a), \tag{16}$$

where $C_3 = \langle R^2_{\rm atom}\rangle/12$ is the plane-mirror Lennard-Jones constant and where the dimensionless function $f(x)$ is

$$f(x) = \frac{6}{(1+x)^3}\left(1+\frac{1}{3}x^2\right) . \tag{17}$$

The function $f(R/a)$ which is plotted in Fig. 1 has the limiting value 1 at the surface of the cavity and 6 at the center. The interaction energy has limits

$$\langle U_I\rangle \;\to\; -\frac{e^2}{4\pi\epsilon_0}\frac{C_3}{(a-R)^3} \quad \text{as} \quad R\to a^- \tag{18}$$
$$\to\; -\frac{e^2}{4\pi\epsilon_0}\frac{6C_3}{a^3} \quad \text{as} \quad R\to 0. \tag{19}$$

References

[1] J. E. Lennard-Jones, Trans. Faraday Soc. **28**, 333 (1932).