INSIGHT INTO THE FORMATION OF MULTIPLY CHARGED FULLERENE CLUSTERS

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Introduction

It may come as a surprise to know that there is currently no stable mathematical solution to the fundamental problem of calculating the electrostatic interaction between two charged particles of a dielectric material. A solution to the problem for two conducting (metallic) particles was first proposed by Lord Kelvin in 1845, and although there are many papers to be found in the literature covering the topic of dielectric particles, all of the solutions presented to date suffer from problems of convergence and/or instability when the particles are in close proximity. However, at close separation there exist distinct regions of space where particles with the same sign of charge are strongly attracted to one another. Since two particles with the same charge should repel one another this pattern of behaviour seems, at first sight, very unusual!

The attraction between particles with the same charge but dissimilar sizes arises through anisotropies in the induced multipole interactions – an effect of significant mathematical complexity especially for dielectric materials, which until now have not been fully understood and described quantitatively. A general solution to the problem of interacting charged dielectric particles has been found and has been shown to exhibit rapid convergence and stability up to the point where particles touch [1].

A quantitative understanding of how charged particles of dielectric materials interact has applications that span much of chemistry, physics, biology and engineering. Areas of interest include cloud formation, ink jet printing and the stability of emulsions. In this work, the solution [1] is applied to study the stability and fragmentation of multiply charged clusters of fullerenes $(C_{60})_n^{z+}$ for the ejection of a singly charged monomer.

Mathematical Solution

A general solution to the problem of two interacting spherical particles of arbitrary size, electrical charge, and dielectric constant is presented, covering a full range of separation distances including the point of contact. The action of charges under their mutual influence is obtained from Gauss's law that couples uniquely the surface potential with the distribution and magnitude of electrical charge on the surface of the spheres. The effect of the surface charge is integrated to obtain an analytical expression for the electrostatic force acting on the spheres at arbitrary separations. The result is a simple series expression for the force that converges rapidly, can be efficiently generalized to many-body systems for studying interactions in concentrated solutions, and can be readily implemented within a variety of particle collision and coalescence models.

The boundary conditions selected for the problem imply a constant charge system in which the total net surface charge on each sphere does not change with a variation in distance between spheres. The total surface charge density on dielectric materials is related to the free and bound charge densities. Since the net charge is fixed and independent of the dielectric constant, variations in the force between dielectric materials is due to induced bound charges on the surfaces of the spheres.

Stability and Fragmentation of $(C_{60})_n^{z+}$: Discussion

In fragmentation of multiply charged clusters of fullerenes $(C_{60})_n^{z+}$, for the ejection of a singly charged monomer to occur the Coulomb repulsion between the molecules must exceed a threshold value for the binding energy of a single C_{60} to a cluster of size n and radius $n^{1/3}$.

Applying the solution [1] to calculate the electrostatic force between two spheres in contact both having dielectric constant of 4.4, which corresponds to the value obtained for fullerenes in thin film measurements [2], we obtain the results shown in Figure 1.

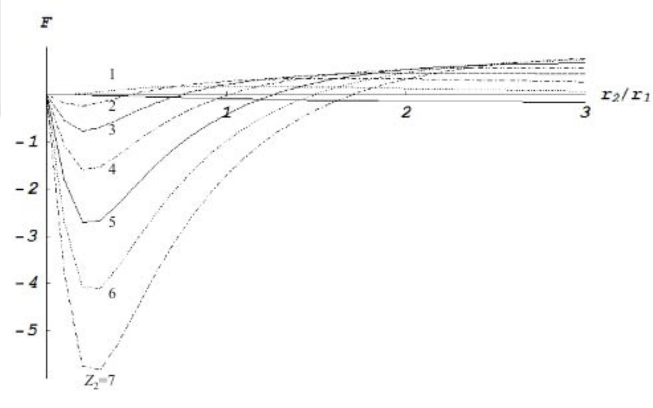

Figure 1. The electrostatic force between two touching spheres as a function of the radius ratio r_2/r_1. Sphere 1 has a charge of z_1 =1, and the charge on sphere 2 varies from z_2=1 to 7. Both spheres have the value of dielectric constant of 4.4.

For spheres of equal ratio of surface charge the repulsive Coulomb force has the greatest value when both spheres are of equal radius. Thus the most favourable ejection would appear to be an even size split. However, for non-equal charges the maximum value of the Coulomb force occurs at increasing values of the radius ratio depending on the charge ratio. The largest repulsive force seen in Figure 1 is for charges of z_2=7 and z_1=1 and r_2/r_1=3. Taking the maximum value of the repulsive force for z_1=1 and $n_{cluster,1}$=1 where $n_{cluster,1}$ is the number of molecules in cluster 1, it is possible to calculate the size of cluster 2 ($n_{cluster,2}$) that gives the largest value of Coulomb repulsion for a given charge. This data fits well with the predictions of the liquid drop model [3] and the experimental observations [4] for the appearance sizes $n_{cluster,2}(z)$ of multiply charged fullerene clusters $(C_{60})_n^{z+}$ (see Table 1).

Table 1. The sizes of multiply charged clusters of $(C_{60})_n^{z+}$

z_2	$n_{cluster,2}(z)$ this model	$n_{cluster,2}(z)$ liquid drop model [3]	$n_{cluster,2}(z)$ experiment [4]
2	7	9	5
3	13	15	10
4	23	23	21
5	31	32	33
6	35	42	-
7	38	54	-

A contour plot of the electrostatic force as a function of the charge and size ratio of two spheres has been calculated for the dielectric constant value of 4.4. The results are presented in Figure 2 showing the mid grey value as zero repulsion, white repulsive regions and black attractive regions of the electrostatic interactions.

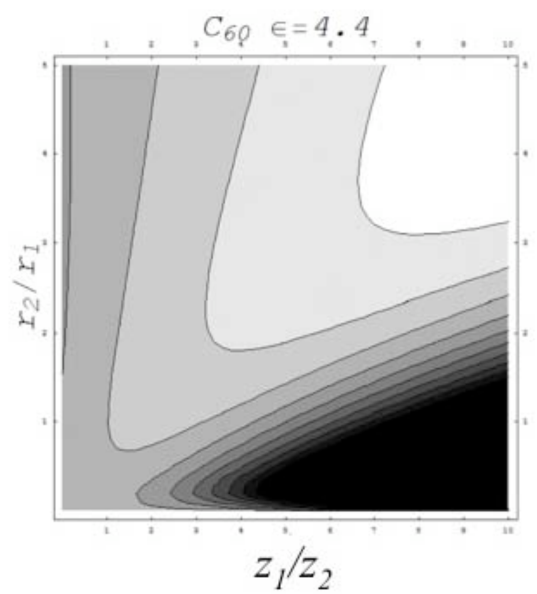

Figure 2. The contour plot for the electrostatic force between two spheres as a function of the radius ratio r_2/r_1 and the charge ratio z_2/z_1, showing repulsive regions (white) and attractive regions (black) of the electrostatic interactions.

Conclusions

The stability and fragmentation of multiply charged clusters of fullerenes $(C_{60})_n^{z+}$ for the ejection of a singly charged monomer has been studied using the newly developed model for calculating the electrostatic interaction between two charged particles of a dielectric material. The comparison with experiments has shown excellent accuracy of the method.

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References

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