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Short Communication

Why like-charged particles of dielectric materials can be attracted to one another

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ABSTRACT

Calculations of surface charge density provide evidence of the physical effects responsible for particles of a dielectric material carrying the same sign of charge being attracted to one another. The results show that attraction requires a mutual polarisation of charge leading to regions of negative and positive surface density close to the point where the particles make contact. These results emphasise the significance of using charged particle models where the surface charge is non-stationary.

1. Introduction

There are many instances in chemistry, physics, biology, and engineering, where charged particles of dielectric materials interact with one another. For particles carrying the same sign of charge there is an interesting, but at the same time very significant, range of relative size and charge, within which, rather than being repelled, the particles can actually be attracted to one another. Examples of systems where such an effect can have an influence on how particles behave include water droplets in clouds [1], dust particles in space [2], and toner particles in electrophotographic printers [3]. Very recently, a new solution has been presented for calculating the electrostatic interaction between two charged dielectric spherical particles [4]. A feature of these new equations is that they converge very rapidly for low values of dielectric constant and are stable up to the point where particles touch. When applied to particles with the same sign of charge, the link between size, charged and the onset of an attractive interaction was found to be very sensitive to the magnitudes of the dielectric constants.

As part of the process of achieving a solution to this problem, it was necessary to describe the surface charge density on each particle [4]. In several previous attempts to address the problem of charged particle interactions, the surface charge density on each particle has been represented as having either a uniform distribution or a non-uniform but static distribution [5–10]. In contrast, other solutions have made the charge density a dynamic quantity that fluctuates in response to changes in separation between particles [11–13]. This latter property is a feature of the solution presented recently by the authors [4], and the purpose here is to utilise that dynamic character of the surface charge density to gain insight as to how particles of the same sign of charge can be attracted to one another. Fig. 1 gives a geometric representation of the problem being addressed. For the purposes of this paper, the diagram has been simplified, but full details can be found in Ref. [4]. What the treatment in Ref. [4] currently neglects is the inclusion of a van der Waals force; however, for pairs of charged particles that contribution appears to be negligible [6], and certainly has no influence on the distribution of surface charge.

For each of the spheres shown in Fig. 1 the total surface charge density can be calculated, and for the case of sphere 1, the appropriate equation is:

$$\sigma_1(\beta_1) = \frac{1}{4\pi K}\sum_{l=0}^{\infty} A_{1,l}\frac{2l+1}{a_1^{l+2}}P_l(\cos\beta_1) \tag{1}$$

where spherical polar coordinates (r_1, β, φ_β) are used to define the vector $\boldsymbol{r}_1$, $P_l(\cos\beta_1)$ are Legendre polynomials, and $K = 1/4\pi\varepsilon_0$, where ε_0 is the permittivity of free space (vacuum). At the surface of sphere 1, $\boldsymbol{r}_1 = \boldsymbol{a}_1$. The coefficients $A_{i,l}$ describe the consequences of mutual polarisation by the two interacting spheres and are a function of their relative dielectric constants (k_1 and k_2), charge (Q_1 and Q_2), radii (a_1 and a_2), and the distance between their centres, h. The relative dielectric constants are defined as $k_i = \varepsilon_i/\varepsilon_0$ where particle i is composed of a dielectric material with a permittivity equal to ε_i. An equation equivalent to (1) can be written for sphere 2 and the exact details of how $A_{1,l}$ and $A_{2,l}$ are calculated can be found in Ref. [4]. As presented in Ref. [4] the equations

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describing the interaction between two charged dielectric particles are applicable to systems of any scale (nano-, micro-, macro-, etc.) as long as they can be represented as spheres.

For the purposes of illustrating how the surface charge density changes in response to an interaction between two particles with the same sign of charge, calculations have been undertaken on two realistic systems. Several recent experiments have examined the stabilities of multiply charged clusters composed of C_{60} fullerenes [14,15], and these are representative of particles with a comparative low relative dielectric constant, $k = 3–4$. The second system examined is that of colliding charged water droplets ($k = 80$), where the process of charge scavenging makes an important contribution to the growth of aerosol droplets in clouds [1,16].

Fig. 2 shows how the charge density changes across the surfaces of two C_{60} molecules that are in contact. In this particular case one of the molecules is neutral and the other carries a charge of +2 and so the circumstances are such that the two molecules should be attracted to one another. For each C_{60} the quantity that has been plotted is $2\pi a_i \sin(\beta_i)\sigma_i(\beta_i)$, where the surface charge density at each point has been weighted by an element of surface area. For the point of contact on each sphere to have a common origin in all of the plots of this nature, the internal angle for the second sphere has been plotted as $\pi-\beta_2$. To achieve uniform curves it was necessary to sum out to $l = 50$ in Eq. (1).

As can be seen, charge density on the neutral C_{60} has become polarised such that it is increasingly negative close to the point of contact and more positive towards $\beta_1 = \pi$; however, the areas under the two components sum to zero. Since this creates a problem regarding normalisation of the plots, the scales in all of the examples shown are arbitrary and only the points at which they might cross from being positive to negative are identified. There is also evidence in Fig. 2 that the surface charge density on the $Q_i = +2$ molecule has been polarised towards the point of contact; however, in this case, $\sigma_2(\beta_2)$ has become more positive. This feature will become more significant when we begin to consider like-charged particles. Fig. 3 shows how charge density on the neutral molecule behaves as a function of separation between the centres of the two spheres. For this particular case, the surface charge eventually becomes uniformly zero across the sphere, however, even when the surfaces are 0.75 nm apart ($h-2a = 0.75$ nm, where $a = 0.38$ nm and is the radius of a C_{60} molecule) the +2 charge continues to exert an influence on the neutral particle.

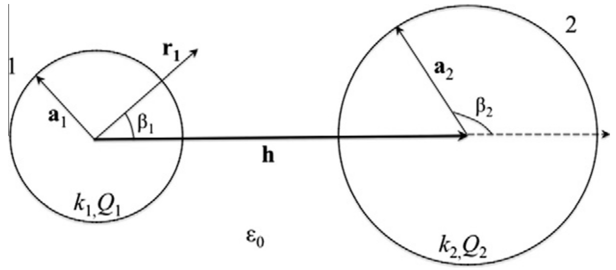

Fig. 1. Geometric representation of two interaction spheres. Dielectric constants, permanent charges and their radii are denoted as k_i, Q_i and $\boldsymbol{a}_i$. The distance of separation of the centres of the spheres is denoted by $\boldsymbol{h}$.

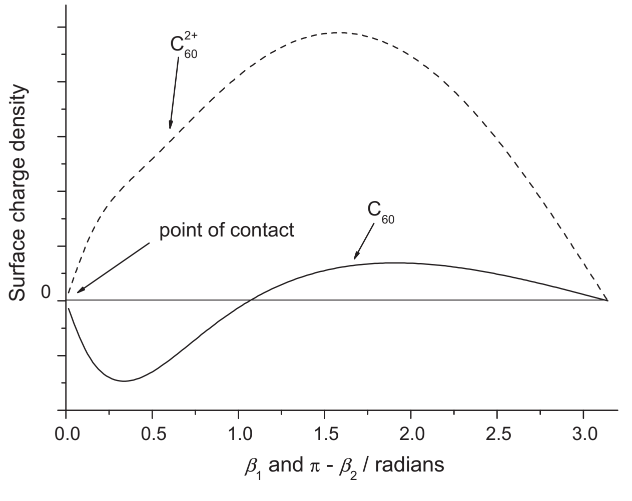

Fig. 2. Plot of calculated surface charge densities on C_{60} and C_{60}^{2+} when in contact as a function of the angles β_1 and $\pi-\beta_2$, respectively. A value of 3.45 has been taken for the dielectric constant k [17].

Both Tong [11], and Allen and Hansen [12] have calculated charge density distributions across the surfaces of interacting spheres, and the latter have shown how the density can vary as a function of sphere–sphere separation. However, neither group has addressed the problem of attraction between like-charged spheres.

Experiments on the stabilities of multiply charged clusters of C_{60} has shown that there are distinct limits below which the clusters are unable to accommodate charge and remain stable [14,15]. One such limit exists for $(C_{60})_n^{3+}$ whereby n, the number of C_{60} molecules, has to be $\geqslant 10$ for the cluster to be stable. Calculations on the $(C_{60})_n^{3+}$ clusters have shown that the fragmentation pathway with the lowest energy barrier involves the loss of a singly charged monomer, C_{60}^+ [17]. Therefore, a collision between C_{60}^+ and $(C_{60})_{n-1}^{2+}$ should be an attractive interaction for $n \geqslant 10$. According to our model, the above interaction becomes attractive at $n = 13$, which matches an earlier calculation by Nakamura and Hervieux [17]. To ensure we are safely either side of that limit, surface charge densities have been calculated for interactions $C_{60}^+ + (C_{60})_5^{2+}$ and $C_{60}^+ + (C_{60})_{14}^{2+}$. To simplify the calculations, a liquid drop model has been adopted, whereby the clusters have been represented as spheres that have volumes equivalent to nC_{60} [17]. Within this model, a calculation of the force [4] that exists between C_{60}^+ and $(C_{60})_5^{2+}$ confirms the presence of a repulsive interaction, whereas for C_{60}^+ and $(C_{60})_{14}^{2+}$ the interaction is attractive. The calculated surface charge densities for $(C_{60})_5^{2+}$ and $(C_{60})_{14}^{2+}$ when they are both in contact with C_{60}^+ are shown in Fig. 4. It can be seen from the

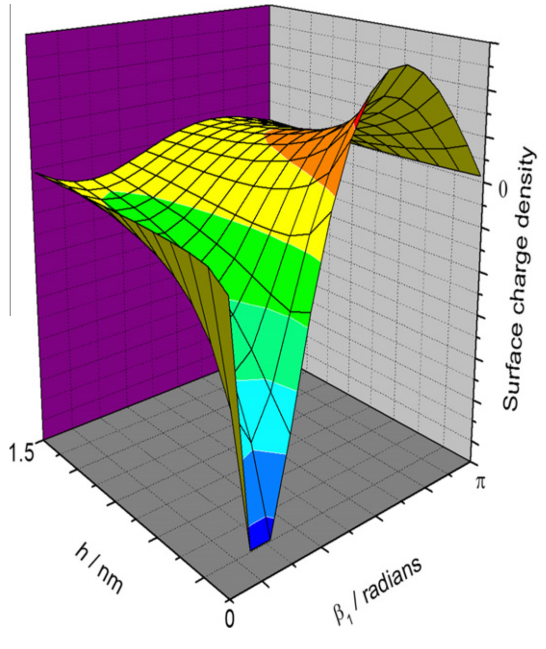

Fig. 3. Plot of the calculated change in surface charge density on C_{60} as a function of both h, the distance of separation from C_{60}^{2+} and β_1.

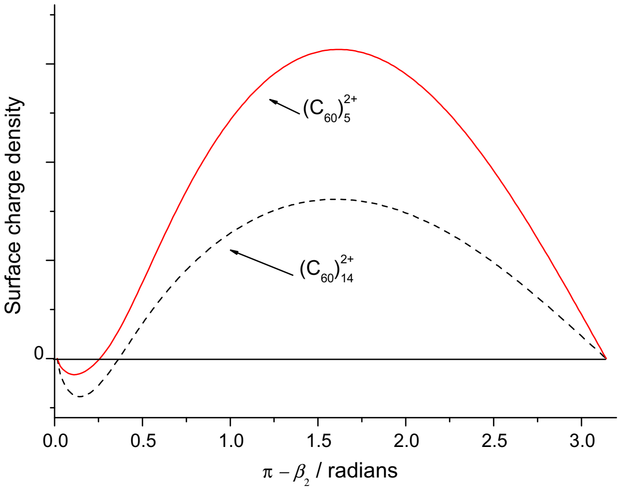

Fig. 4. Plot of calculated surface charge densities on $(C_{60})_5^{2+}$ and $(C_{60})_{14}^{2+}$ as a function of the angle $\pi-\beta_2$ when either of the two clusters is in contact with C_{60}^+.

results that the much higher charge density of the C_{60}^+ fragment has polarised charge on the remaining cluster to create a small region of negative charge density close to the point where the fragments touch.

Although the magnitude of the response to C_{60}^+ is different for each of the two larger clusters, the fact that they both show a similar pattern of behaviour would suggest that this alone is not sufficient to differentiate between an attractive and a repulsive interaction. Fig. 5 shows how, in each case, C_{60}^+ responds to the interaction. These curves show evidence of a marked difference in behaviour between the two systems. In the case of $C_{60}^+ + (C_{60})_{14}^{2+}$, charge density on C_{60}^+ has been polarised towards the point of contact, and there is evidence of an increase in density at around $\beta_1 = 0.5$. In contrast, $C_{60}^+ + (C_{60})_5^{2+}$ shows the reverse behaviour with the surface charge density on C_{60}^+ being repelled away from the point of contact. The areas under the two curves in Fig. 5 are equal and remain fixed irrespective of the value of *h*.

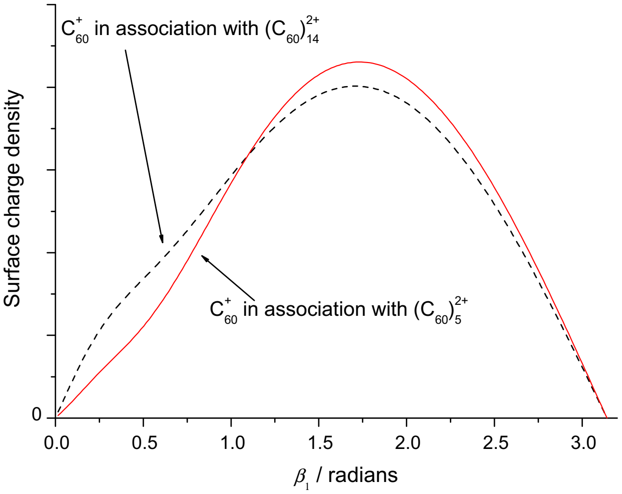

Fig. 5. Plot of the calculated surface charge densities on C_{60}^+ following contact with either $(C_{60})_5^{2+}$ or $(C_{60})_{14}^{2+}$ as a function of the angle β_1.

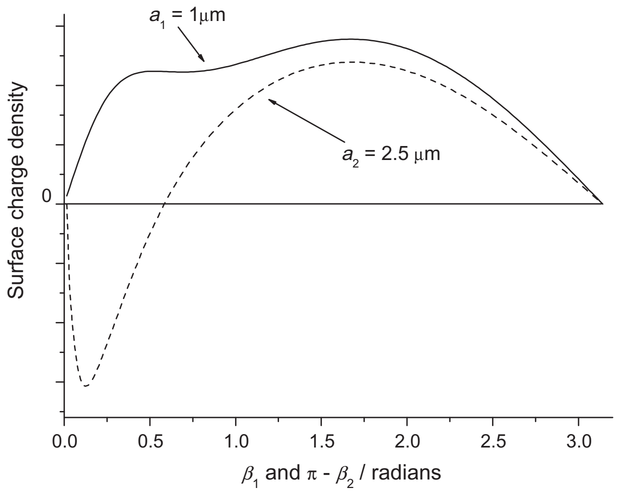

Fig. 6. Plot of calculated surface charge densities on two water droplets when in contact ($a_1 = 1$ µm; $a_2 = 2.5$ µm) as a function of the angles β_1 and $\pi-\beta_2$, respectively. A value of 80 has been taken for the dielectric constant, *k*, and the charge on each droplet is +200.

The final system to be examined is one associated with the interaction of water droplets and the mechanism of charge scavenging in rain clouds [1,16,18]. Under certain conditions, droplets with the same sign of charge are attracted to one another thereby creating a larger droplet carrying a greater amount of charge. Fig. 6 shows the result of a surface charge calculation involving two droplets with radii of 1 µm and 2.5 µm and each carrying a charge of +200. A room temperature value, $k = 80$, has been taken for the dielectric constant and again, a calculation of the force between the particles [4] confirm that two such droplets would be attracted to one another.

As can be seen from Fig. 6, the system exhibits patterns of behaviour that are similar to those found for the much smaller fullerene clusters; namely, that charge density on the larger species is strongly polarised in those regions of the sphere that are close to the point of contact. At the same time, the less polarisable (smaller) of the two species also shows evidence of significant (positive) charge displacement towards the point of contact. This process appears to be driven entirely by differences in charge density on the surfaces of the two spheres as they begin to make contact. Finally, Fig. 7 shows how the surface charge density on the larger of the droplets responds to an increase in separation between the particles. The gradual loss of negative density close to the point of contact is balanced by a decline in positive charge density on the opposite side of the sphere. Once the surfaces are approximately

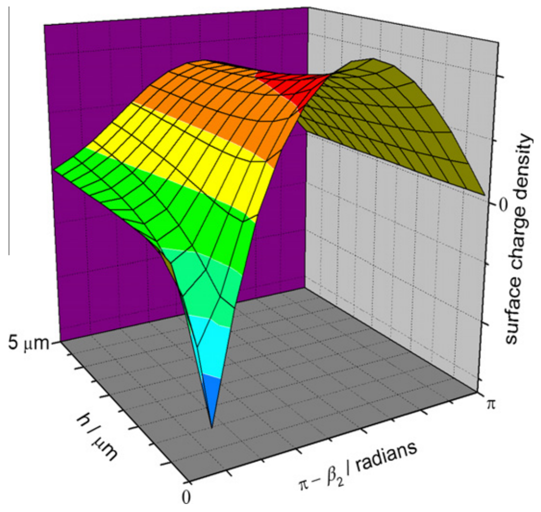

Fig. 7. Plot of the calculated change in surface charge density on a water droplet ($a_2 = 2.5$ µm) as a function of both *h*, the distance of separation from a second droplet, and $\pi-\beta_2$.

1.5 µm apart the charge density begins to adopt the hemispherical uniformity expected of an isolated sphere.

From an examination of all of the systems presented here it can be seen that attraction between spherical particles carrying the same sign of charge, requires a mutual polarisation of charge density close to the region where the spheres make contact. To generate an attractive interaction between like-charged particles it is not sufficient for one species with a high charge density to polarise another, there has to be a reciprocal displacement of density on the second particle. A dynamic surface charge density, which responds to particle separation as shown, for example in Figs. 3 and 7, could have interesting implications for the time-dependent behaviour of solvent molecules when charge particles are suspended in a liquid medium. Over the duration of a particle–particle collision, any polar solvent molecules in close proximity to either particle will come under the influence of transient changes in surface charge, which it turn, could result in a temporary realignment of the molecules. For large particles, collision lifetimes are likely to be quite long which could increase the chances of detecting any such realignment.

Although the model as formulated [4] does allow for the inclusion of a solvent medium (*via K*) this does not apply to an electrolyte where the attraction between, for example, charged stabilised colloidal particles, is not due entirely to polarisation effects. A treatment of the electrical double layer created by the presence of charged particles in an electrolyte requires a different approach to the one we have outlined here [19].

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