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Charge and size of a ring in an electrolyte with atomic force microscopy

Daniel Lazarev, Fredy R. Zypman*

Yeshiva University, New York, NY 10033, USA

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ABSTRACT

We study the interaction force between a ring with a dipole density and the tip of an Atomic Force Microscope. Given the vector nature of a dipole we study the force for all possible dipole orientations. These results are applied to the practical problem of a charged ring electrically partially shielded by ions in an electrolyte. We provide theoretical tools to analyze experiments and extract parameters such as the charge and size of the ring, the screening, and the Debye length.

1. Introduction

An object embedded in an electrolyte has its charge shielded by the counterions in solution. Thus, any instrument aimed at measuring the charge of the object must account for the electrostatic problem that includes the embedding electrolyte. Here we are interested in understanding the response of the Atomic Force Microscope (AFM) to a charged ring immersed in an electrolyte, a ubiquitous case in soft matter in which all or part of the ring's charge is shielded by the ions in the medium [1–3]. The problem of how to use the AFM to measure size and charge of nano-rings in air has already been solved [4]. This work extends that result to the most relevant case of the AFM with fluid cells [5–7]. Thus the methods developed in this article should be of use to measure static charge in liquid. This liquid could be of explicit interest such as is the case in electrochemistry or in biological buffers, but also due to its implicit presence as humidity when nominally making measurements in air. From a fundamental electrostatic standpoint, we obtain for the first time the electrostatic field produced by the interaction of the ring of charge with the liquid and the spherical tip of the AFM.

We first consider two rings of opposite charges characterized by an electric dipole density. We analyze two specific configurations for oppositely charged near rings—one *stacked*, in which one ring is vertically above the other, and the second *concentric*, with one ring inside the other on the same horizontal plane. We further show that the electric field produced by a system comprised of two oppositely charged near rings of arbitrary orientation can always be treated as a linear combination of the stacked and concentric cases.

Integrating over all such orientations we obtain the AFM forces for a bare charged ring dressed by ionic charge. Since in a practical situation this dressing generally produces partial screening, the total force on the AFM is obtained as the sum of the force produced by a bare ring of charge and that produced by a dipole ring of charge, modulated by a parameter representing the particular ionic conditions of the surrounding electrolyte.

A note on notation used: Since the experimental quantity accessible in AFM is the vertical force on the tip, the electric field and force expressions we consider in this paper are all in the *z*-direction. To simplify the notation, we will not write the subscript "*z*." In addition, the stacked case quantities are labeled '$\boxminus$,' while the concentric case quantities are indicated by '$\odot$.'

The paper is organized as follows. In section 2, Theory, we briefly review, in subsection 2.1, the case of a single charged ring as it is necessary to introduce notation. Subsections 2.2 and 2.3 already get into the systems focus of this paper, the stacked and concentric ring configurations. Section 3 presents the derivation of forces for both cases mentioned above. Subsection 3.3 shows a proof that a force in a generic configuration can always be written as a linear combination of the cases studied in section 3. Section 4 is an application of the results for the case of a ring embedded in an electrolyte. Section 5 shows how in practice to obtain dipole and size of the ring from the AFM force measurements. Section 6 presents experiments that have used AFM to study ring structures ranging in size from $\mathring{A}$ to microns. 7 is the conclusion section.

* Corresponding author.
E-mail address: zypman@yu.edu (F.R. Zypman).

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2. Theory

2.1. Charged ring

In this subsection we briefly state the results for electric field and AFM force generated by a ring of charge. This problem has already been solved [4], but we succinctly show the salient features of that analysis to introduce notation and relevant results needed for this article.

For a single ring of radius A and total charge Q, the electric field in the z-direction at $(x,\ 0, z)$ is given by

$$E(A,x,z) = \frac{Q}{(2\pi)^2\varepsilon}\frac{z}{\left(x^2+z^2+A^2\right)^{\frac{3}{2}}} f[\mu(A,x,z)], \tag{1}$$

where μ and $f(\mu)$ are defined by

$$\mu = \frac{2Ax}{x^2+z^2+A^2} \tag{2}$$

$$f(\mu) = -\frac{2\mathbb{E}\left(\frac{2\mu}{1+\mu}\right)}{(\mu-1)\sqrt{1+\mu}}, \tag{3}$$

with $\mathbb{E}(m)$ the Elliptic Integral of the Second Kind [8], and ε the medium's permittivity [9]. To find the force on the AFM tip with radius of curvature R (Fig. 1) due to the ring, we evaluate the electric field at a point on the image ring, $x = B = \frac{AR^2}{A^2+d^2}$ and $z = d - d' = d - \frac{R^2}{A^2+d^2}d$, multiply by 2π to obtain the total field acting on the image ring, and finally multiply by the image charge, which gives:

$$F^0 = -F_0\frac{\eta\beta^2}{\sqrt{\beta^2+\eta^2}}\left\{\frac{1-\frac{1}{\beta^2+\eta^2}}{\left[\beta^2+\left(\frac{\beta}{\beta^2+\eta^2}\right)^2+\left(\eta-\frac{\eta}{\beta^2+\eta^2}\right)^2\right]^{\frac{3}{2}}}\right\}f(\mu), \tag{4}$$

where $\eta \equiv \frac{d}{R}$, $\beta \equiv \frac{A}{R}$, and $F_0 \equiv \frac{\lambda^2}{\varepsilon_0}$, λ being the linear charge density on the ring. F^0 is then the force corresponding to zero ion concentration. For the two-ring systems described in the Introduction, Equation (1) will be the starting point.

2.2. Stacked ring configuration

This geometry corresponds to two near rings of equal diameters exactly above each other (Fig. 2). Taking ring 1 (red) in Fig. 2 to be positive, and ring 2 (blue) negative, the electric field due to the former is $E^+_{\boxminus} = E(A,\ x,\ z)$, while the field due to the latter is $E^-_{\boxminus} = -E(A,\ x,\ z - L_{\boxminus})$, where the function E is defined in Equation (1).

The total vertical electric field at a point $P = (x,\ 0,\ z)$ is $E_{\boxminus} = E^+_{\boxminus} + E^-_{\boxminus}$. Expanding this expression as a power series in $L_{\boxminus}$, and keeping terms to first order in $L_{\boxminus}$, gives

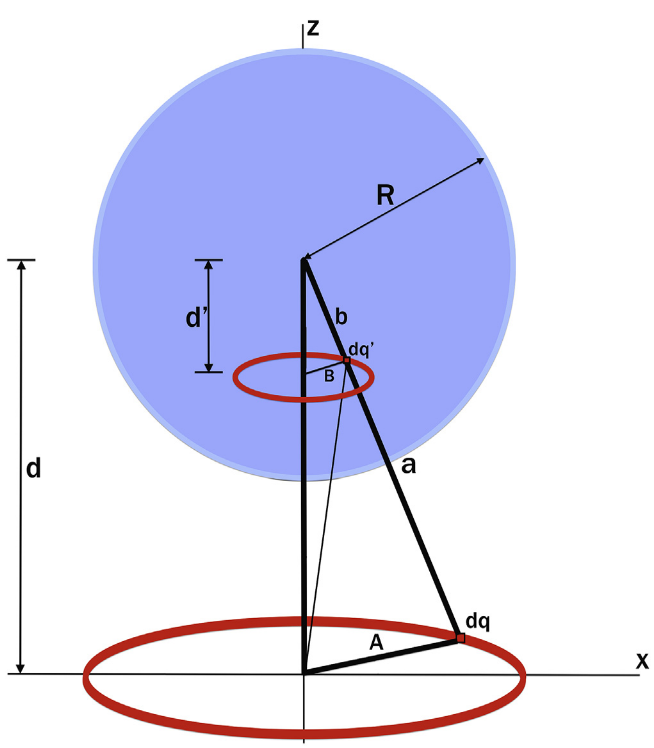

Fig. 1. A ring of radius A near an AFM tip with radius of curvature R produces an image ring of radius B.

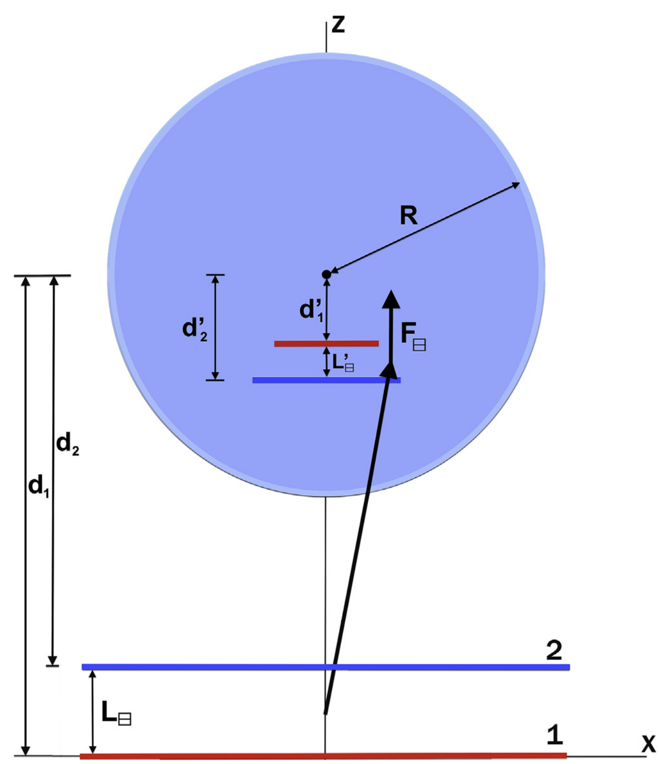

Fig. 2. Sagittal view of the stacked ring setup near an AFM tip, and the resulting image rings. The lines labeled "1" and "2" are rings of opposite charge, lying on the horizontal plane. The image rings inside the sphere are shown with slightly different radii, but in the limit $L_{\boxminus} \to 0$ they overlap.