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Electrostatic interactions in strongly coupled soft matter

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Abstract

Charged soft-matter systems—such as colloidal dispersions and charged polymers—are dominated by attractive forces between constituent like-charged particles when neutralizing counterions of high charge valency are introduced. Such counter-intuitive effects indicate strong electrostatic coupling between like-charged particles, which essentially results from electrostatic correlations among counterions residing near particle surfaces. In this paper, the attraction mechanism and the structure of counterionic correlations are discussed in the limit of strong coupling based on recent numerical and analytical investigations and for various geometries (planar, spherical and cylindrical) of charged objects.

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1. Introduction

Electrostatic interactions and processes involving electric charges appear ubiquitously in biological and soft-matter systems. Electric charges make materials water-soluble and lead to many important technological and biological applications. In industry, for example, the stability of colloidal dispersions is often a desirable property as in the case of paints and food emulsions such as milk. One way to stabilize colloidal suspensions against coagulation or flocculation (occurring due to attractive van-der-Waals forces) is to generate long-range repulsive interactions between constituent colloidal particles by imparting permanent like-charges to these particles [1–3], or by grafting charged polymeric chains to their surfaces (forming hairy particles or polymeric brushes) [4]. Charged polymers, or the so-called *polyelectrolytes*, and their synthesis have also attracted a lot of attention [5] since, due to their water-solubility, they offer a useful option in design and processing of non-toxic environment friendly materials. In biology, on the other hand, electrostatic effects emerge in many striking examples such as the DNA-packaging process in the cell nucleus. In each human cell, a total length of about 2 m of DNA—which bears a total negative charge of about $10^{10}e$ (i.e., one elementary charge, e, per 1.7 Å)—is stored inside the cell nucleus with a diameter of less than 10 μm. This storage process involves a hierarchical structure on the lowest level of which, short segments of DNA are tightly wrapped around positively charged proteins of few-nanometer size (the so-called Histones). It is shown experimentally [6] that such a tightly wrapped state is only stable for intermediate, physiological salt concentrations, at which an optimal balance between self-repulsion of DNA segments and the DNA-Histone attraction is achieved.

Charged macromolecules (macroions) in solution are always surrounded by neutralizing counterions, and also in general by coions. Counterions form electrostatically bound clouds in the proximity of macroions and in many cases, predominantly determine the electric properties of charged solutions [3]. In particular, counterions can alter the effective interaction between like-charged macroions, and may generate a dominant electrostatic attraction between them in certain physical conditions [7–78]. Like-charge attraction manifests itself in a number of famous examples, namely, the condensation of DNA molecules [10], bundle formation of stiff polymers [16] and aggregation of colloidal particles [32–34]. Interestingly, such an attraction emerges only in *strongly coupled* systems, e.g. when macroions are highly charged (with surface charge densities up to $1e/\mathrm{nm}^2$ as in the DNA system), neutralizing counterions are multivalent, or when the temperature or the dielectric constant of medium is low. For instance, the DNA condensation process, in which long DNA molecules condense into a tightly packed, circumferentially wound torus, is observed in experiments where multivalent counterions (such as trivalent spermidine ions) are introduced [10]. A similar trend has also been found in numerous numerical simulations of like-charged membranes, colloids and polymers [19–42], where highly charged macroions are found to form closely packed bound states due to attractive forces of electrostatic origin. These attractive forces are of typically large strength compared to the usual van-der-Waals