BULL. AUSTRAL. MATH. SOC. 80A30
VOL. 15 (1976), 149-150.

Abstracts of Australasian PhD theses

Dispersion forces between macroscopic bodies: effects due to electrolyte and geometry

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This thesis is divided into six chapters. The first of these is an introductory chapter, intended to provide a background for the next five chapters, and to put the subject matter and the methods used into perspective. The main thrust of the thesis is in the second, third, and sixth chapters; the fourth chapter being an appendix to the third, and the fifth an introduction to the sixth.

The second chapter introduces the topic of spatial dispersion, and the question of additional boundary conditions is examined. Explicit expressions are obtained for the allowed electromagnetic modes in a film of spatially dispersive medium, in the case of a particular additional boundary condition, and for a very general class of dielectric constants. The full retarded dispersion free energy of two spatially dispersive half spaces interacting across a slab of non spatially dispersive material, and the opposite case of a film of spatially dispersive material, is calculated for a particular form of the dielectric constant. For the former case it is found that spatial dispersion is unimportant unless the separation of the half-spaces is comparable with characteristic lengths associated with spatial dispersion.

In the remaining chapters the particular example of spatial dispersion

Received 22 March 1976. Thesis submitted to the Australian National University, May 1975. Degree approved, February 1976. Supervisors: Dr Brian Davies, Professor B.W. Ninham.

provided by electrolytes is examined. In Chapter 3 the interaction of two planar double layers is considered by a formalism due to Craig. Besides obtaining many old results which are unified by this approach, some new results emerge, including an extra long range repulsion, which can give a significant correction to the classical expressions. The appendatory chapter, Chapter 4, indicates how the low surface charge methods considered in Chapter 3 may be extended to arbitrary surface charges.

The final chapters, 5 and 6, are concerned with the effect of geometry on the interaction in electrolyte. In Chapter 5 we calculate the interaction free energy of two spheres in terms of spherical harmonic wave-functions, and indicate a possible method of solution of Helmholtz's equation using bispherical wave-functions. The distance dependence of the interaction energy of two polarizable dipoles is obtained as a special case. This chapter also provides an introduction to the more general considerations of the last chapter.

We develop in Chapter 6 a perturbation expansion from an integral equation solution of Helmholtz's equation, which is suitable for use when the interacting bodies, which, though required to be smooth, may be of arbitrary shape, are close together. Some old results are recovered, and we present analytical expressions for the leading terms in the interaction between bodies of cylindrical, spherical and elliptic-paraboloidal geometrical shape. In addition, we calculate curvature corrections to the Onsager-Samaras result for the effect of electrolyte on the surface tension of ionic solutions. Some numerical estimates are reported.