On the cross-over from Casimir (retarded) to London (non-retarded) van der Waals interactions

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The experimental measurement of surface forces between plates a distance L apart stands as the most important probe for the understanding of van der Waals intermolecular forces [1]. Paradoxically, experiments have had far less trouble confirming these forces in the long range (Casimir) retarded regime, where they decay as L^{-3}, than in the familiar non-retarded regime (London-Hamaker), where they decay as L^{-2}. Be as it may, in most applications in chemical-physics, from wetting to colloidal sciences, the retarded Casimir regime is completely ignored, in favor of the non-retarded London-regime [2]. The reason is that the full theoretical treatment for the interaction between two semi-infinite media across a dielectric due to Dzialoshinskii, Lifshitz and Pitaevskii (DLP) is numerically very difficult to implement, and analytically not very transparent to interpret [3, 4]. Unfortunately, using merely the pair-wise Hamaker approximation can incur in very serious errors, as the crossover from London to Casimir regimes is often accompanied by a sign reversal of the forces [3, 4].

In this communication we present simple closed forms for the distance dependent Hamaker constant, that are able to capture with great accuracy all the relevant regimes from the subnanometer length-scale to beyond the micrometer [5]. The theory uses dielectric data as only input and does not require any adjustable parameter. This allows an easy implementation of DLP theory, but more importantly, it allows us to clearly recognize the widely different L dependence that results as the distance between plates is increased. Particularly, for the finite frequency contributions to the Hamaker constant, we show how the exact treatment provides an L^{-2} regime at short distance, an L^{-3} regime at intermediate distance, but also the very much less appreciated e^{-L} exponential suppression of finite frequency contributions that can lead to sign reversal of the Hamaker constant (see Fig. 1).

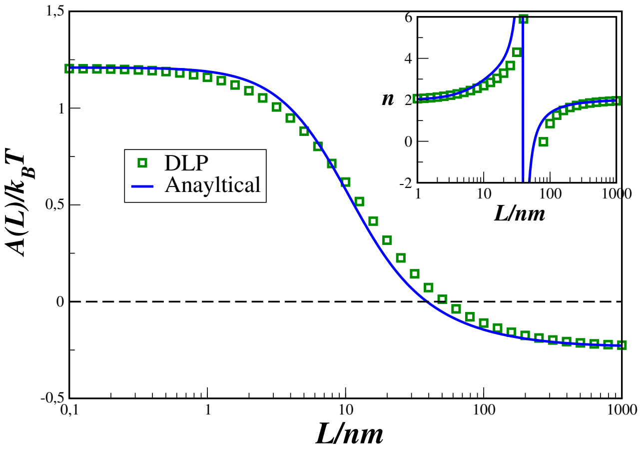

Fig. 1. Hamaker constant of an octane film adsorbed between water and air. The symbols are numerical results from DLP theory, the line is a simple analytical approximation with no adjustable parameters. The crossover from non-retarded to retarded interactions results in the sign reversal of the Hamaker constant. Inset displays the effective exponent of the power law decay.

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