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Investigation of the range of validity of the pairwise summation method applied to the calculation of the surface roughness correction to the van der Waals force

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ABSTRACT

It has long been recognized that stochastic surface roughness can considerably change the van der Waals (vdW) force between interacting surfaces and particles. However, few analytical expressions for the vdW force between rough surfaces have been presented in the literature. Because they have been derived using perturbative methods or the proximity force approximation the expressions are valid when the roughness correction is small and for a limited range of roughness parameters and surface separation. In this work, a nonperturbative approach, the effective density method (EDM) is proposed to circumvent some of these limitations. The method simplifies the calculations of the roughness correction based on pairwise summation (PWS), and allows us to derive simple expressions for the vdW force and energy between two semispaces covered with stochastic rough surfaces. Because the range of applicability of PWS and, therefore, of our results, are not known *a priori*, we compare the predictions based on the EDM with those based on the multilayer effective medium model, whose range of validity can be defined more properly and which is valid when the roughness correction is comparatively large. We conclude that the PWS can be used for roughness characterized by a correlation length of the order of its rms amplitude, when this amplitude is of the order of or smaller than a few nanometers, and only for typically insulating materials such as silicon dioxide, silicon nitride, diamond, and certain glasses, polymers and ceramics. The results are relevant for the correct modeling of systems where the vdW force can play a significant role such as micro and nanodevices, for the calculation of the tip-sample force in atomic force microscopy, and in problems involving adhesion.

1. Introduction

The vdW[1] force is an important component contributing to the total force between two surfaces separated by distances in the nanometric scale. For this reason it is of relevance, for instance, in the problem of adhesion [1,2], for the interpretation of AFM force measurements [3], in the modeling of nanoelectromechanical systems [4,5] and in many other branches of physics, chemistry, biology and engineering [6,7]. In the particular case of nanoelectromechanical systems and AFM, which involve the interaction between solid bodies separated by vacuum, air or other gases, only the dispersive component of the vdW force is relevant. An adequate theoretical understanding of such systems, where the vdW force may be of relevance, requires a correspondingly adequate theoretical evaluation of the dispersive component of vdW force. For that purpose, several methods have been developed that take into account its dependence upon the materials, through their dielectric function or polarizability, and on the geometry of the interacting bodies [7–9]. Similarly to many other physical problems both perturbative [10] or computational methods, based on the continuum [7,11] or atomistic model of the interacting bodies [12,13], have been developed to address the nontrivial problems. However, except for specific geometries or material properties, these methods do not provide us with convenient analytical expressions for the free energy or force

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[1] List of abbreviations: Atomic force microscope (AFM); cumulative distribution function (CDF); effective density model (EDM); multilayer effective medium model (MEMM); probability distribution function (PDF); proximity force approximation (PFA); polystyrene (PS); pairwise summation (PWS); root means square (rms); van der Waals (vdW); ultra-violet (UV); list of symbols used frequently: average separation between two rough surfaces (a); distance of closest approximation between two rough surfaces (b); distance between two polarizable particles (r); vdW free energy per unit of area (E); vdW pressure (P); Hamaker constant (H); temperature (T); probability distribution function (p); volume fraction or cumulative distribution function (f); dielectric function (ϵ); semispace i (S_i); rms amplitude of surface roughness (σ); correlation length (Λ).

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that can be easily evaluated for applications such as the interpretation of AFM tip-sample force measurements. It is only for the case of two planar or slightly tilted or curved surfaces that comparatively simple expressions for the vdW force can be found that account for the material properties and geometry of the interacting bodies. In these cases the force is obtained using the Lifshitz theory [8] in conjunction with the Derjaguin or proximity force approximation (PFA), which assumes that the total force can be obtained integrating the force over a surface that is sufficiently smooth to be considered as piecewise plane. This simple approach has been used, for instance, to determine the vdW force between a suspended bar nanoresonator and an underlying planar substrate [4,5], between a probe tip, of comparatively large radius, and a planar sample surface in AFM [14], and between a colloidal particle and a plane surface [15].

We note, however, that when analyzed in more detail an important characteristic of surfaces of nanodevices, AFM probe tips, and colloidal particles is the presence of surface roughness which, in general, cannot be accounted for by the methods presented above. The surface roughness is known to have the potential to significantly alter the vdW force [15]. In spite of its relevance, there is no general model that provides an analytical expression that allows one to calculate exactly the effects of surface roughness for arbitrary surface roughness profile and surface separation. The first attempts to model the effect of surface roughness were made by van Bree et al. [16] and relied on the use of pairwise summation (PWS). This approach was later used by other authors to obtain, for instance, the roughness correction for the force between a spherical particle and a semi-infinite medium [17] and the corrected tip-sample force in AFM [18]. While a widely used method of calculation of the vdW force for non-trivial geometries, usually providing comparatively simple analytical expressions for the vdW force, PWS is criticized because the method does not take into account many-body effects and retardation in a consistent manner. More importantly, its range of applicability is not known *a priori*. More rigorous methods, that take into account many-body effects and retardation, have been developed by Maradudin and Mazur [19], Maia Neto et al. [20], and Wu and Schaden [21]. A common feature in these works is that they treat the problem perturbatively, the results being limited to lower order in the perturbative expansion. For this reason the results of Maradudin and Mazur [19] are valid under the quite restrictive condition $\sigma \ll \Lambda \ll a$, where σ denotes the rms roughness amplitude, Λ the roughness correlation length, and a the mean surface separation. The results of Maia Neto et al. [20] represent an improvement over those of Maradudin and Mazur [19] and are valid for $\sigma \ll \Lambda, a$. Finally, the most recent results of Wu and Schaden [21] are only limited by the restriction $\sigma \ll a$. We can see that all these perturbative approaches have in common that their results are valid for $\sigma \ll a$. Because all approaches predict that the roughness correction is, at least approximately, proportional to σ/a, the results are valid only when the roughness correction is comparatively small. In fact, within their range of validity, the corrections predicted by either of the perturbative approaches amount to a maximum of approximately 20% of the final force. From the three approaches, only that of Maradudin and Mazur provides a comparatively simple approximate analytical expression for the vdW force. In the other two approaches, the derivation of the final force is more involved, and approximate analytical expressions can be obtained only in limiting cases.

It is interesting to note that while the approaches of Maradudin and Mazur [19] and that of Maia Neto et al. [20] predict an increase of the force with the decrease of Λ, the predictions of Wu and Schaden [21] go in the opposite direction. All these methods, however, agree in the limit of small σ/Λ ratio, where PFA applies. These contradictory results have established a controversy which is relevant for the validity of another method proposed to calculate the roughness correction, namely, the multilayer effective medium model (MEMM)[22–24]. This method adopts the point of view that the virtual electromagnetic waves that are responsible for the vdW force interact with the rough surface as if it were an effective medium, resulting from the mixing of the intervening medium (vacuum or water, for example) and the solid material at the surface. As discussed in Ref. [23] the MEMM was conceived to give reliable results for rough surfaces characterized by σ of the order of Λ. This idea was first proposed and briefly explored by Maradudin and Mazur [19], who modeled the rough surface as a single layer comprised of an effective medium whose effective dielectric properties they have derived using their own physical model. A single effective medium layer was also used later to model the rough surface [15]. In this last case the effective dielectric function was obtained using the well known Clausius–Mosotti mixing rule and the energy was calculated using the equations for a layered system, previously derived in extensions of the Lifshitz theory. Extending this previous work, Dagastine et al. [22] formulated a multilayer model in which the rough surface was divided into several layers. Each layer had its effective dielectric function obtained using the Rayleigh mixing rule and the vdW force was calculated using the formalism for multilayers developed by Ninham and Parsegian [6,25]. In their work, Dagastine et al. [22] have also compared the predictions of their MEMM with experimental results for the free energy for the interaction of a polystyrene (PS) sphere with a plane substrate of glass or PS. While the qualitative agreement between theory and experiment shows a significant improvement in the case of glass–PS interaction, in the case of PS–PS interaction a significant discrepancy can still be observed. Therefore, while the experimental work of Dagastine et al. [22] evidences the strong effects of surface roughness on the vdW force, we cannot conclude that it fully corroborates the predictions based on the MEMM. Further theoretical analysis of the results of Dagastine et al. [22] and more experimental investigation of the effects of short-scale roughness are required to validate the MEMM, as well as the other approaches proposed for the calculation of the roughness effect.

The relevance of the MEMM, as stated by Gusso and Reis [23], comes from the fact that it represents the first method that allows the calculation of the roughness correction for the case of short scale roughness, characterized by Λ of the order of σ. Short scale roughness has been found, for instance, in SiO_2 beads as illustrated in Fig. 1, and in silicon AFM tips coated with diamond-like carbon and ultrananocrystalline diamond as illustrated in Fig. 6 of Ref. [26]. It is worth noting that the MEMM can predict the vdW force when it is expected to be most affected by the surface roughness. In accordance with the results of Maradudin and Mazur [19] and Maia Neto et al. [20], the model predicts a significant increase in the vdW force when compared to the predictions of PFA.

It was due to this expected large contribution of short-scale roughness to the vdW force that one of the authors investigated the contribution of short-scale roughness at the probe tip to the tip-sample force in AFM [24]. One interesting result of this investigation was the very good agreement, obtained at short separations, between the predictions of the MEMM and those from simple approximate analytical expressions derived using PWS. This result motivated the present investigation.

The PWS is a widely used method of calculation of the vdW force. It has been used for systems of various geometries and dimensions [27,28]. The great advantage of the method resides in its mathematical simplicity. It can provide comparatively simple analytical expressions for the vdW force for various complex geometries [27]. The method has been used previously to derive approximate analytical expressions for the roughness correction [16–18], which are quite simple. However, in spite of being used for calculations of the vdW force in scales ranging from atomic [12,13,26] to micrometric scale [17], the range of validity of PWS is not known *a priori*, a situation that may prevent the correct usage of these very simple and convenient analytical expressions. For example, while PWS has