

The Role of Long Range Forces on Surface Free Energies

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As the surface to volume ratios diminish in miniaturized devices, surface effects become increasingly important. Unfortunately, calculation of surface free energies by computer simulation is a rather difficult matter. 1) The standard procedure based on explicit evaluation of the pressure tensor poses conceptual problems, particularly when constraint forces are involved. 2) Explicit account of long range forces, whether dispersive or coulombic is difficult, to the point that they are ignored or dealt only approximately in many instances. In this talk we will present recent results which allow one to circumvent both of these difficulties. On the one hand, we develop a methodology for the calculation of surface free energies based on the probability distribution of a wandering interface. Similar to the Test Area method, this procedure has the advantage of avoiding altogether explicit evaluation of the virial. On the other hand, we apply numerical long range corrections which allow one to account fully for the long range nature of the interactions. We discuss the effect of semi infinite slices beyond the simulation box, which are usually neglected, and develop a methodology which allows one to account for this effect reliably. The methods are applied for the evaluation of surface and interfacial tensions of different systems.

[1] L. G. MacDowell and P. Bryk, *Phys. Rev. E*, **75**, 061609, (2007).

[2] F. J. Blas, L. G. MacDowell, E. de Miguel, G. Jackson, *J. Chem. Phys.* **129**, 144703 (2008)