Electric-field mapped averageing for dielectric constant

The dielectric constant of a material under given conditions is the ratio of permittivity or capacitance to that of vacuum. Dielectric constant is very important to a variety of technological applications. In physical chemistry, the dielectric constant is of particular interest because it quantifies how the solvent attenuates electrostatic interactions of solutes, and thus greatly it greatly influences the solution properties. Accordingly, the calculation of dielectric constants of model fluids is an important application of molecular simulation. However, using standard methods, this calculation is difficult to accomplish accurately and precisely. Harmonically mapped averaging is an efficient technique for evaluating the anharmonic energy/pressure in for crystal system. We generalize this method to other forms of mapped averages, and in particular we apply this idea to formulate a new method to evaluate the dielectric constant from molecular simulation. The development is based on the interaction of rigid dipoles with an external field E. The dielectric constant is the second derivative of the free energy with respect to external field, which can be expressed in terms of the variance of fluctuations of the dipole moment of the system. Calculation of fluctuation-based quantities always has large errors, and this problem afflicts the standard approach to calculation of the dielectric constant. The mapped average is instead built on knowledge of fluctuations in noninteracting dipoles, such that the simulation measures only contributions in excess of this. We compare the results of these two approaches in both hard-sphere and Lennard-Jones systems. The comparison shows the mapped average to be much more precise for the same amount of computation.

Key words: dielectric constant, mapped average