

Shell model Simulations

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David Fincham discussed the calculation of the pressure in the shell model of polarisable ions. In this model ions are represented by a “core” and a “shell”, both carrying charges, and connected by a harmonic spring. In the “ideal” shell model the shells have zero mass, and relax instantaneously to zero force positions. In shell-model molecular dynamics using the “adiabatic” method of Mitchell and Fincham (*J. Phys.: Condes. Matter* 5 (1993) 1031) the shells have a small mass, and their motion is integrated by normal m.d techniques. The ion is therefore treated exactly as if it were a diatomic molecule. However, the shell mass is chosen small enough that the spring frequency remains well above the lattice vibrational frequencies. In these circumstances the core-shell internal degree of freedom does not thermalise and its temperature remains very low. This ensures that the results agree with the ideal model.

Since the internal degree of freedom is not in thermal equilibrium with the other degrees of freedom, it is preferable to approach the pressure calculation from a mechanical rather than a thermodynamic point of view. Such an approach may be based on the virial theorem, which is derived in the textbooks of Hansen and McDonald and of Haile using arguments only from classical mechanics: One can then decide to apply the virial theorem either to the “diatomic molecules” (ions) or to the “atoms” (core and shell). In the “molecule” approach the kinetic term involves only the centre-of-mass (COM) or translational kinetic energy, and the virial term involves COM separations and total molecule-molecule forces. In the “atoms” approach one must include the internal kinetic energy as well as the translational kinetic energy. The virial term includes the virial of the “bonds” as well as the atom-atom intermolecular terms.

The “molecule” and “atom” approaches must agree when ensemble averages are taken. However, a stronger statement can be made. In the ideal (zero shell mass) shell model, the two approaches give identical instantaneous pressures. This is because the shells are always in zero force positions, and then the bond virial is cancelled by the term which converts from the atom-atom to the centre-centre virial. In the adiabatic shell model the two methods give instantaneous pressures which are still equal to an excellent degree of approximation. The details will appear in a forthcoming publication by Fincham, Mackrodt and Mitchell.