Project A – Lab 4

Lab 4 involved perturbing atoms form their stable state and then easing them back into a stable state using steepest descent and conjugate gradient methods to minimise the total energy function. This was done for a Neon crystal (which is modelled with using Lennard Jones potential) and a MgO crystal (which is modelled using Buckingham Coulomb potential).

Neon Crystal

The derivative required for both the steepest descent and conjugate gradient and conjugate gradient algorithms was found analytically to be:

$$\frac{\partial E}{\partial x^i} = \sum_{j \neq i} 24\varepsilon \left(\frac{2\sigma^{12}}{{r_{ij}}^{14}} - \frac{\sigma^6}{{r_{ij}}^8}\right) x^i$$

Where x^i is the x coordinate of the i'th atom, r_{ij} is the distance between atoms i and j with periodic boundary conditions applied while ε and σ are the constants from the Lennard-Jones equation found here to be $\varepsilon = 3.083 \times 10^{-3} eV$ and $\sigma = 2.782$ A

The crystal was perturbed by shifting every atom by up to 10% of the lattice constant in a random cardinal direction. The minimisation algorithm was then run until the gradient was found to be sufficiently small. In both cases line minimisation was carried out using the secant method meaning a hyperparameter sigma must be chosen. The values in the code were found empirically to balance speed of convergence with accuracy of convergence, increasing or decreasing sigma (in the code called smolNum) such that finer adjustments can be made when the gradient is smaller in magnitude.

In the case of Lennard Jones potential, steepest descent was found to converge quickest likely since it must calculate the gradient (which must be done in a for loop and is hence quite expensive).

MgO Crystal

The derivative for the Buckingham Coulomb potential was found analytically to be:

$$\frac{\partial E}{\partial x^i} = \sum_{j \neq i} \frac{1}{4\pi\varepsilon_0} \left(\frac{q_i q_j}{{r_{ij}}^3}\right) x^i + \sum_{j \neq i,\, q_i, q_j \neq 0} \left(\frac{A\rho}{r_{ij}} e^{-\frac{r_{ij}}{\rho}} - \frac{6C}{{r_{ij}}^8}\right) x^i$$

Where $\varepsilon_0 = 8.854 \times 10^{-12} Fm^{-1}$, $q = \pm 1.7e$ with A, ρ and C being constants from the Buckingham Coulomb equation given as $A = 4870, \rho = 0.2670A, C = 77$ for O^- interactions and $A = 926.69, \rho = 0.29909A, C = 0$.

When running conjugate gradient, a value for hyperparameter sigma that gave quick convergence could not be found and consequently it was much slower than the steepest descent method.

Conclusion

Since a hyperparameter must be tuned for both methods and conjugate gradient is the most sensitive to that hyperparameter, steepest descent minimised the energy quicker for both Lennard Jones potential and Buckingham Coulomb potential.

References

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[2] Henkelman, Graeme and Uberuaga, Blas P. and Harris, Duncan J. and Harding, John H. and Allan, Neil L. MgO addimer diffusion on MgO(100): A comparison of ab initio and empirical models. American Physical Society. p. 115437. 2005. https://journals.aps.org/prb/abstract/10.1103/PhysRevB.72.115437