Problem set 7: Computational Molecular Physics and Methods of Molecular Simulations

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1. Time reversibility

(10 points) Prove that the original Verlet scheme is time-reversible.

2. Molecular vibrations

(25 points) A few typical vibrational wavenumbers of diatomic fragments

- $C-H$: $\omega/(2\pi c) \approx 3000$ cm^{-1}
- $C-C$: $\omega/(2\pi c) \approx 1000$ cm^{-1}
- $C=C$: $\omega/(2\pi c) \approx 1700$ cm^{-1}
- $C\equiv C$: $\omega/(2\pi c) \approx 2200$ cm^{-1}
- $I-I$: $\omega/(2\pi c) \approx 215$ cm^{-1}

Set up a harmonic oscillator model and solve the following tasks

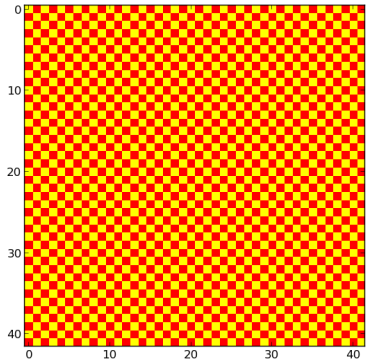
- Look up the definition of "'wavenumbers"' and convert the values given above into frequencies [Hz] and vibrational periods [s].
- Calculate the reduced masses and the force constants.
- Discuss the influence of the masses and and the strength of the respective chemical bonds.
- What would be a reasonable time step for numerical integration of the equations of motions of the harmonic oscillators? How does it change for the different harmonic oscillators?

3. Poisson equation (Thursdays lectures)

(10 points) Consider a 42 by 42 grid with spacing of one. On each grid point a charge of either +1 or -1 is located such that signs are alterating, see figure below. Solve the Poisson equation

$$\nabla^2 \phi_i(\mathbf{r}) = -\frac{\rho_i(\mathbf{r})}{\epsilon_0} \tag{1}$$

by discretising the Laplace-Operator ∇^2 and plot the electrostatic potential ϕ_i on the grid points.



4. Ewald Summation (Thursdays lectures)

(20 points) In Ewald summation the electrostatic interactions are split onto a short-range and a long -range term, the first of which is solved in real space, the latter in reciprocal, k-space:

$$\begin{aligned} E &= E^S + E^L - E^{\text{self}} \\ &= \frac{1}{8\pi\epsilon_0} \sum_{\mathbf{n}} \sum_{i=1}^{N} \sum_{i=1}^{N} {}^{*} \frac{q_i q_j}{|\mathbf{r}_i - \mathbf{r}_j + \mathbf{n}L|} \text{erfc}\left(\frac{|\mathbf{r}_i - \mathbf{r}_j + \mathbf{n}L|}{\sqrt{2}\sigma}\right) \\ &\quad + \frac{1}{2V\epsilon_0} \sum_{\mathbf{k}} |S(\mathbf{k})|^2 \frac{\mathrm{e}^{-\sigma^2 k^2/2}}{k^2} \\ &\quad - \frac{1}{2\epsilon_0 \sigma (2\pi)^{3/2}} \sum_{i=1}^{N} q_i^2 \end{aligned} \tag{2}$$

In order to compute Eq. (2) efficiently, we must truncate the infinite sums. We would like to control the error made by this, both in the real-space and in the reciprocal space sum.

1. What is the number of ions N_c contained within a cutoff sphere of $R_c$with uniform number density N/V ?

2. For the k-space sum we choose wave-vectors according to $\mathbf{k} = \frac{2\pi}{L}(i, j, k)$. What is the number N_k of index triples in reciprocal space?

3. Set cutoff radius $R_c$and k-space cutoff K_c such that the cutoff errors are given by $\exp(-\mathrm{p})$:

$$\text{erfc}(\frac{r}{\sqrt{2}\sigma}) \mid_{r=R_c} \approx \exp\left(-R_c^2/2\sigma^2\right) = \exp(-\mathrm{p})$$

   and

$$\exp\left(-\sigma^2 K_c^2/2\right) = \exp(-p)$$

   Give an expression for the total execution time as function of R_c if the time to evaluate one ion pair is t_r in real space and t_k in k-space (Hint: express K_c in terms of R_c and p)

4. Compute the optimal cutoff radius that solves the Electrostatics problem with error tolerance e^{-p} in minimal total execution time (with fixed particle density N/V)