Sommersemester 2019, Struktur und Simulation

Übung: Calculating gradients and forces

Assignment due date: 22.4.2019

In this exercise, we will go through all the steps of deriving a expression for a force from a potential energy function. This will involve taking some derivatives. If it's been a long time since you've calculated a derivative this might look scary, but with a little practice it shouldn't be too difficult. We will first repeat some things already mentioned in the lectures and try to clear up any misunderstandings. Then we will go through some gradient calculations step by step. Finally, there is a homework assignment where you will calculate some gradients yourself.

1 Notation

A vector $\vec{r}$

$$\vec{r} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

has Euclidean length r

$$r = \sqrt{x^2 + y^2 + z^2}$$

Mathematicians call the length a "norm" (there are other norms apart from the Euclidean norm, but that's not important here).

The unit vector $\hat{r}$ (it has a length of 1) in direction $\vec{r}$ is given by

$$\hat{r} = \frac{\vec{r}}{r}$$

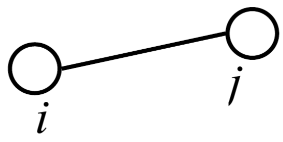
We will use the convention $\vec{r_{ij}} = \vec{r_i} - \vec{r_j}$.

2 Gradient of the length of a vector

Many potential energy functions are functions of distances, which means we will need the gradient of the length of a vector later on. The gradient (∇ or $\frac{\partial}{\partial \vec{r}}$) of the Euclidean length turns out to have the simple form:

$$\nabla r = \frac{\partial}{\partial \vec{r}} r = \frac{\vec{r}}{r} = \hat{r}$$

3 Calculating forces: harmonic bonds



Many potential energy functions are functions of distances. A simple example is the harmonic potential for bonds. Given a harmonic bond between particles i and j, the potential energy is

$$U(r_{ij}) = \frac{k}{2}\left(r_{ij} - r_0\right)^2$$

where k and r_0 are force constants.

As mentioned above $\vec{r_{ij}} = \vec{r_i} - \vec{r_j}$.

If we want to work out the gradient $\nabla_{\vec{r_i}} U(r_{ij})$, we have to use the chain rule:

$$\nabla_{\vec{r_i}} U(r_{ij}) = \left(\frac{d}{dr_{ij}} U(r_{ij})\right)\left(\nabla_{\vec{r_i}}\, r_{ij}\right) = k(r_{ij} - r_0)\frac{\vec{r_{ij}}}{r_{ij}}$$

The force $\vec{F_i}$ acting on particle i is

$$\vec{F_i} = -\nabla_{\vec{r_i}} U(r_{ij}) = -k(r_{ij} - r_0)\frac{\vec{r_{ij}}}{r_{ij}}$$

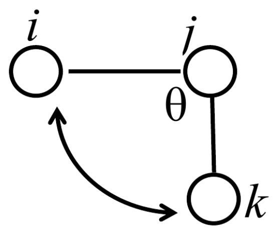
For particle j, we have

$$\nabla_{\vec{r_j}}\, r_{ij} = -\frac{\vec{r_{ij}}}{r_{ij}}$$

and therefore the force $\vec{F_j}$ acting on particle j is

$$\vec{F_j} = -\nabla_{\vec{r_j}} U(r_{ij}) = k(r_{ij} - r_0)\frac{\vec{r_{ij}}}{r_{ij}} = -\vec{F_i}$$

4 Calculating forces: angle potentials



A more complicated energy function is the potential energy for bond angles

$$U(\vec{r_i}, \vec{r_j}, \vec{r_k}) = \frac{k}{2} \left(\cos\theta_{ijk} - \cos\theta_0\right)^2$$

The cosine of the angle θ_{ijk} is

$$\cos\theta_{ijk} = \frac{\vec{r_{ij}} \cdot \vec{r_{kj}}}{r_{ij}\, r_{kj}} = \hat{r_{ij}} \cdot \hat{r_{kj}}$$

Here we have used the dot product $\vec{a} \cdot \vec{b}$ between vectors

$$\vec{a} \;=\; \begin{pmatrix} a_1 \\ \vdots \\ a_M \end{pmatrix}$$

$$\vec{b} \;=\; \begin{pmatrix} b_1 \\ \vdots \\ b_M \end{pmatrix}$$

which is given by

$$\vec{a} \cdot \vec{b} = \sum_{k=1}^{M} a_k b_k$$

The dot product is also called the scalar or inner product.

To calculate the gradient of the bond angle potential, we again use the chain rule:

$$\nabla_{\vec{r_i}} U = \left(\frac{d}{d\cos\theta_{ijk}} \frac{k}{2} \left(\cos\theta_{ijk} - \cos\theta_0\right)^2 \right) \nabla_{\vec{r_i}} \cos\theta_{ijk} = k \left(\cos\theta_{ijk} - \cos\theta_0\right) \nabla_{\vec{r_i}} \cos\theta_{ijk}$$

So we are left with computing $\nabla_{\vec{r_i}} \cos\theta_{ijk}$. Using the definition for $\cos\theta_{ijk}$ from above and the quotient rule, we get

$$\nabla_{\vec{r_i}} \cos\theta_{ijk} = \nabla_{\vec{r_i}} \frac{\vec{r_{ij}} \cdot \vec{r_{kj}}}{r_{ij}\, r_{kj}} = \frac{\vec{r_{kj}}\, r_{ij}\, r_{kj} - \vec{r_{ij}} \cdot \vec{r_{kj}} r_{kj} \hat{r_{ij}}}{r_{ij}^2\, r_{kj}^2} = \frac{1}{r_{ij}} \left(\hat{r_{kj}} - \left(\hat{r_{ij}} \cdot \hat{r_{kj}} \right) \hat{r_{ij}} \right)$$

Here we have used the fact that

$$\nabla_{\vec{a}} \left(\vec{a} \cdot \vec{b} \right) = \vec{b}$$

Substituting $\cos\theta_{ijk} = \hat{r_{ij}} \cdot \hat{r_{kj}}$, we get

$$\nabla_{\vec{r_i}} \cos\theta_{ijk} = \frac{1}{r_{ij}} \left(\hat{r_{kj}} - \cos\theta_{ijk} \hat{r_{ij}} \right)$$

We can do a similar calculation to get $\vec{F_k} = -\nabla_{\vec{r_k}} U$, and then calculate $\vec{F_j}$ with the help of

$$\vec{F_i} + \vec{F_j} + \vec{F_k} = 0$$

5 Checking gradients with the gradient theorem

As you have seen, there are many possibilities for subtle errors when calculating gradients. The gradient theorem can help us check a gradient numerically.

Given a function U and its gradient ∇U, the line integral between any two points $\vec{a}$ and $\vec{b}$ is equal to the difference of the function U evaluated at the endpoints:

$$\int_{\vec{a}}^{\vec{b}} (\nabla U(\vec{r})) \cdot d\vec{r} = U(\vec{b}) - U(\vec{a})$$

As before, the $\cdot$ is a dot product.

Discretising the line integral, we get:

$$\sum_{k=0}^{N-1} (\nabla U(\vec{r_k})) \cdot \vec{\Delta r} \approx U(\vec{b}) - U(\vec{a})$$

with

$$\Delta\vec{r} = \frac{\vec{b} - \vec{a}}{N}$$

and

$$\vec{r_k} = \vec{a} + k\,\vec{\Delta r}$$

For large N, the error should become very small if we implemented the gradient ∇U correctly.

6 Assignment

1. For the harmonic bond potential, the force $\vec{F_i}$ was

$$\vec{F_i} = -k(r_{ij} - r_0)\frac{\vec{r_{ij}}}{r_{ij}}$$

   What is the length of $\vec{F_i}$?

   Hint: what is the length of $\frac{\vec{r_{ij}}}{r_{ij}}$?

2. Show that

$$\nabla r = \frac{\vec{r}}{r}$$

   where the vector $\vec{r}$ has components

$$\vec{r} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

   and length

$$r = \sqrt{x^2 + y^2 + z^2}$$

3. Show that
$$\nabla_{\vec{a}} \left(\vec{a} \cdot \vec{b}\right) = \vec{b}$$
We used this formula when we calculated the gradient for the bond angle potential.

4. Calculate the gradient $\nabla_{\vec{r_i}} U(r_{ij})$ of the Lennard-Jones potential
$$U(r_{ij}) = 4\epsilon \left(\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^{6} \right)$$
Hint: use the chain rule as we did for the harmonic bond potential. This means you only have to calculate $\frac{d}{dr_{ij}} U(r_{ij})$ and then combine it with the gradient $\nabla_{\vec{r_i}}\, r_{ij}$ to get the final answer.

5. Implement the harmonic bond potential. In `/home/petersen/teaching/sus/1_forces` you can find the python scripts `forces.py` and `force_test.py`. Add code to `forces.py` and test the forces with `python force_test.py -v`.

   `force_test.py` tests the forces using the gradient theorem as described in section 5. Take a look at the source code. The script tests the forces for the harmonic bond, Lenard-Jones and angle potential. It fails in each case unless the corresponding force is correctly implemented.

   If you think your implementation is correct but the test still fails, you can change the number of steps, which are hard coded in the test script. There is always a numeric error which depends on the step size and which decreases if you increase the number of steps. However, the given number of steps and accuracy requirement should generally be adequate.

Bonus assignments (optional)

1. Implement the other forces in `forces.py`.