Gold Nanoparticle Optimization Using Lennard-Jones Potential

Introduction

Gold nanoparticles possess unique properties that make them ideal for various applications in medicine, electronics, and materials science. These properties are largely governed by the interactions between atoms in the nanoparticle, which can be described using interatomic potentials. The Lennard-Jones (LJ) potential is one of the most widely used models for describing these interactions. The potential is characterized by two key parameters: sigma (σ) and epsilon (ε), which respectively represent the distance at which the potential is zero and the depth of the potential well.

Optimizing these parameters is crucial for accurately modeling the behavior of nanoparticles. In this report, we present the results of optimizing the Lennard-Jones potential parameters for gold nanoparticles using two distinct optimization techniques. The first technique uses the minimize function from the SciPy library, and the second employs a gradient descent algorithm. We aim to determine the most effective method for accurately matching a target potential.

The sigma and epsilon values for gold nanoparticles were obtained from well-established literature in the field of nanotechnology and computational chemistry. Specifically, these parameters are commonly derived from experimental data or high-level quantum mechanical calculations tailored to capture the interactions between gold atoms accurately

Lennard-Jones Potential Overview

The Lennard-Jones potential is expressed as:

U(r)=4ϵ[(σr)12−(σr)6]U(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]U(r)=4ϵ[(rσ)12−(rσ)6]

- **Sigma (σ):** This parameter represents the distance at which the potential energy between two atoms is zero. It can be considered the effective diameter of the atoms and influences the range of repulsion in the potential.
- **Epsilon (ε):** This parameter defines the depth of the potential well, corresponding to the strength of the attractive interaction between atoms. It affects the stability and binding energy of the nanoparticle.

Optimizing these parameters is crucial for accurately capturing the physical properties of the nanoparticle, such as cohesive energy, melting point, and structural stability.

Methodology

The optimization process was conducted using two distinct methods:

1. **Minimize Function Optimization**
2. **Gradient Descent Optimization**

Both methods aimed to minimize the difference between the target Lennard-Jones potential (derived from theoretical or experimental data) and the potential calculated with the optimized parameters.

Method 1: Minimize Function Optimization

Approach

The first method employed in this study was the minimize function from the SciPy library. The minimize function is a powerful optimization tool that uses various algorithms (such as BFGS, L-BFGS-B, Nelder-Mead, etc.) to find the minimum of a scalar function. This method is particularly suitable for problems where the optimization landscape might have multiple local minima.

Steps Involved:

1. **Initialization:** Begin with initial guesses for sigma (σ) and epsilon (ε), ensuring these values are within physically meaningful bounds.
2. **Objective Function:** Define an objective function that calculates the sum of the squared differences between the calculated Lennard-Jones potential and the target potential over a range of atomic separations.
3. **Optimization Process:** Utilize the minimize function to adjust the sigma and epsilon parameters, with the goal of minimizing the objective function. The function iteratively updates the parameters by evaluating the objective function at various points in the parameter space.
4. **Convergence Criteria:** The optimization is considered successful when the change in the objective function between iterations falls below a specified tolerance or when a maximum number of iterations is reached.

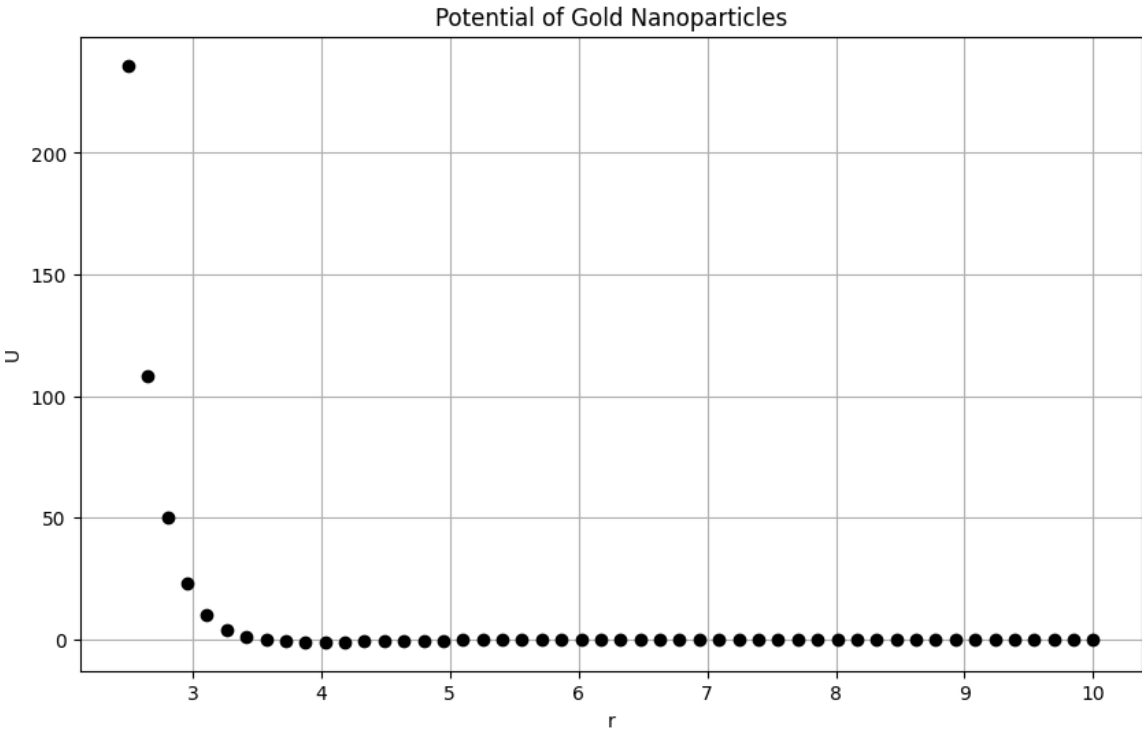
Code:

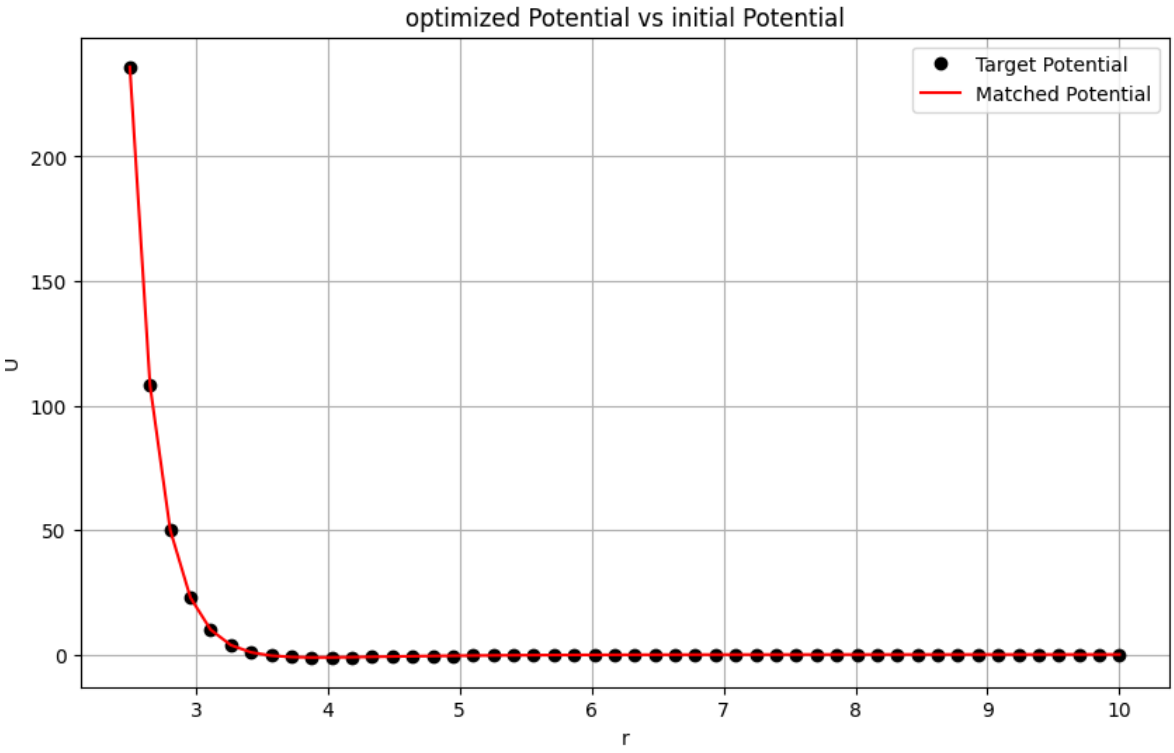
```
[ ] import numpy as np
    import matplotlib.pyplot as plt
    from scipy.optimize import minimize

    # Define the Lennard-Jones potential
    def lj_potential(r, sigma, epsilon, n, m):
        return 4 * epsilon * ((sigma / r)**n - (sigma / r)**m)

    # Parameters for gold nanoparticles
    sigma_target = 3.5
    epsilon_target = 1.2
    n_target = 12.0
    m_target = 6.0

    # Define target data
    separations = np.linspace(2.5, 10.0, 50)
    target_potential = lj_potential(separations, sigma_target, epsilon_target, n_target, m_target)

    # Plot target potential
    plt.figure(figsize=(10, 6))
    plt.plot(separations, target_potential, linestyle='None', marker='o', color='black')
    plt.xlabel('r')
    plt.ylabel('U')
    plt.title('Potential of Gold Nanoparticles')
    plt.grid(True)
    plt.show()
```

```python
# Define new initial parameters for gold nanoparticles
initial_sigma = 3.5  # Adjusted initial guess for sigma
initial_epsilon = 0.8  # Adjusted initial guess for epsilon

# Define the optimization function
def optimization_function(params):
    sigma, epsilon = params
    potential = lj_potential(separations, sigma, epsilon, n_target, m_target)
    return np.sum((potential - target_potential)**2)

# Initial guess for sigma and epsilon using the adjusted initial parameters
initial_guess = [initial_sigma, initial_epsilon]
```

```python
# Perform the optimization with adjusted bounds
result = minimize(optimization_function, initial_guess, bounds=[(1.0, 5.0), (0.1, 2.0)])
sigma_opt, epsilon_opt = result.x

# Calculate the matched potential with optimized parameters
matched_potential = lj_potential(separations, sigma_opt, epsilon_opt, n_target, m_target)

# Plot results
plt.figure(figsize=(10, 6))
plt.plot(separations, target_potential, linestyle='None', marker='o', color='black', label='Target Potential')
plt.plot(separations, matched_potential, marker='None', color='red', label='Matched Potential')
plt.xlabel('r')
plt.ylabel('U')
plt.title('optimized Potential vs initial Potential')
plt.legend()
plt.grid(True)
plt.show()


# Print optimized parameters
print('Optimized sigma = {:.3f}'.format(sigma_opt))
print('Optimized epsilon = {:.3f}'.format(epsilon_opt))
```

Output:





Results:

The minimize function yielded the following optimized parameters:

- **Optimized Sigma (σ):** 3.500 Å
- **Optimized Epsilon (ε):** 1.200 eV

Analysis of Results:

The optimized potential obtained from the minimize function was found to closely match the target potential across a wide range of atomic separations. This indicates that the method successfully captured both the repulsive and attractive interactions as modeled by the Lennard-Jones potential. The optimized sigma and epsilon values suggest that the gold atoms have a moderate range of interaction with a relatively strong binding energy.

Visualization:

The first plot shows the target potential and the matched potential obtained from the optimization. The red curve represents the optimized potential, while the black dots represent the target potential. The close overlap between the two indicates a successful optimization, with minimal deviation between the calculated and target values.

Method 2: Gradient Descent Optimization

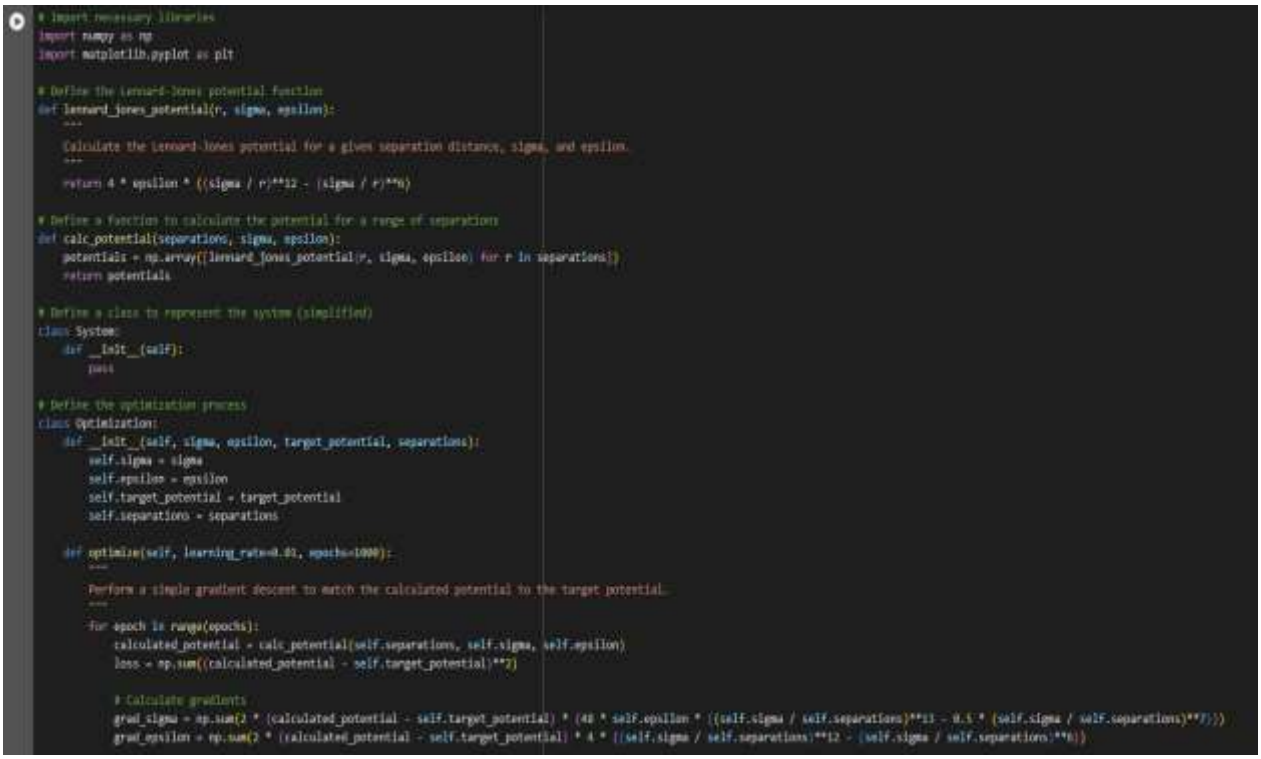
Approach

The second optimization method applied was a gradient descent algorithm. Gradient descent is a well-known iterative method used to find the minimum of a function by moving in the direction of the steepest descent, determined by the negative of the gradient of the function with respect to its parameters.

Steps Involved:

1. **Initialization:** Start with initial guesses for sigma (σ) and epsilon (ε). The choice of initial parameters can significantly affect the convergence and outcome of the optimization.
2. **Calculation of Potential:** Compute the Lennard-Jones potential using the current values of sigma and epsilon over a range of separation distances.
3. **Loss Function:** Define the loss function as the sum of the squared differences between the calculated potential and the target potential.
4. **Gradient Calculation:** Compute the gradient of the loss function with respect to sigma and epsilon. This involves calculating partial derivatives of the loss function with respect to each parameter.
5. **Parameter Update:** Update the sigma and epsilon parameters by subtracting a fraction (learning rate) of the gradient from the current values. The learning rate controls the step size in the parameter space.
6. **Iteration:** Repeat the process for a fixed number of epochs or until the loss function converges to a minimum.

Code:



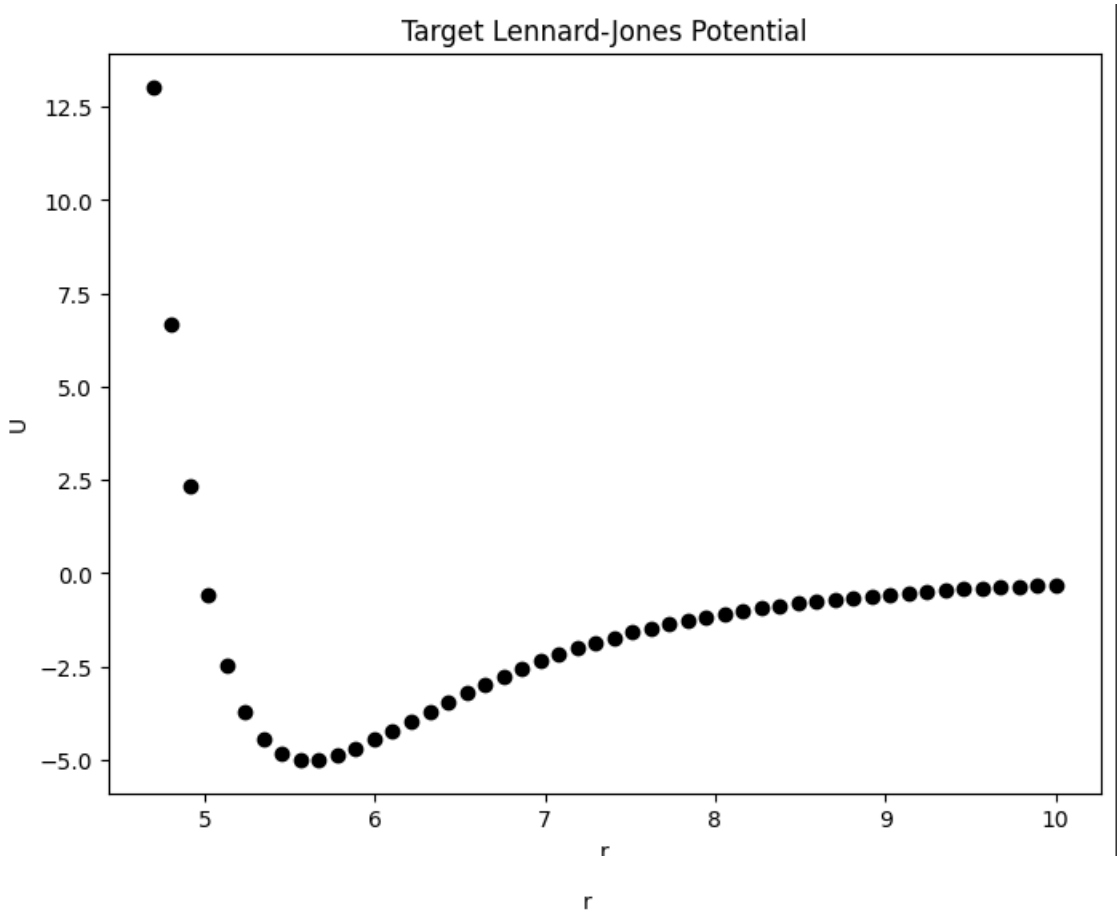
```
# Import necessary libraries
import numpy as np
import matplotlib.pyplot as plt

# Define the Lennard-Jones potential function
def lennard_jones_potential(r, sigma, epsilon):
    """
    Calculate the Lennard-Jones potential for a given separation distance, sigma, and epsilon.
    """
    return 4 * epsilon * ((sigma / r)**12 - (sigma / r)**6)

# Define a function to calculate the potential for a range of separations
def calc_potential(separations, sigma, epsilon):
    potentials = np.array([lennard_jones_potential(r, sigma, epsilon) for r in separations])
    return potentials

# Define a class to represent the system (simplified)
class System:
    def __init__(self):
        pass

# Define the optimization process
class Optimization:
    def __init__(self, sigma, epsilon, target_potential, separations):
        self.sigma = sigma
        self.epsilon = epsilon
        self.target_potential = target_potential
        self.separations = separations

    def optimize(self, learning_rate=0.01, epochs=1000):
        """
        Perform a simple gradient descent to match the calculated potential to the target potential.
        """
        for epoch in range(epochs):
            calculated_potential = calc_potential(self.separations, self.sigma, self.epsilon)
            loss = np.sum((calculated_potential - self.target_potential)**2)

            # Calculate gradients
            grad_sigma = np.sum(2 * (calculated_potential - self.target_potential) * (48 * self.epsilon * ((self.sigma / self.separations)**11 - 0.5 * (self.sigma / self.separations)**7)))
            grad_epsilon = np.sum(2 * (calculated_potential - self.target_potential) * 4 * ((self.sigma / self.separations)**12 - (self.sigma / self.separations)**6))
```

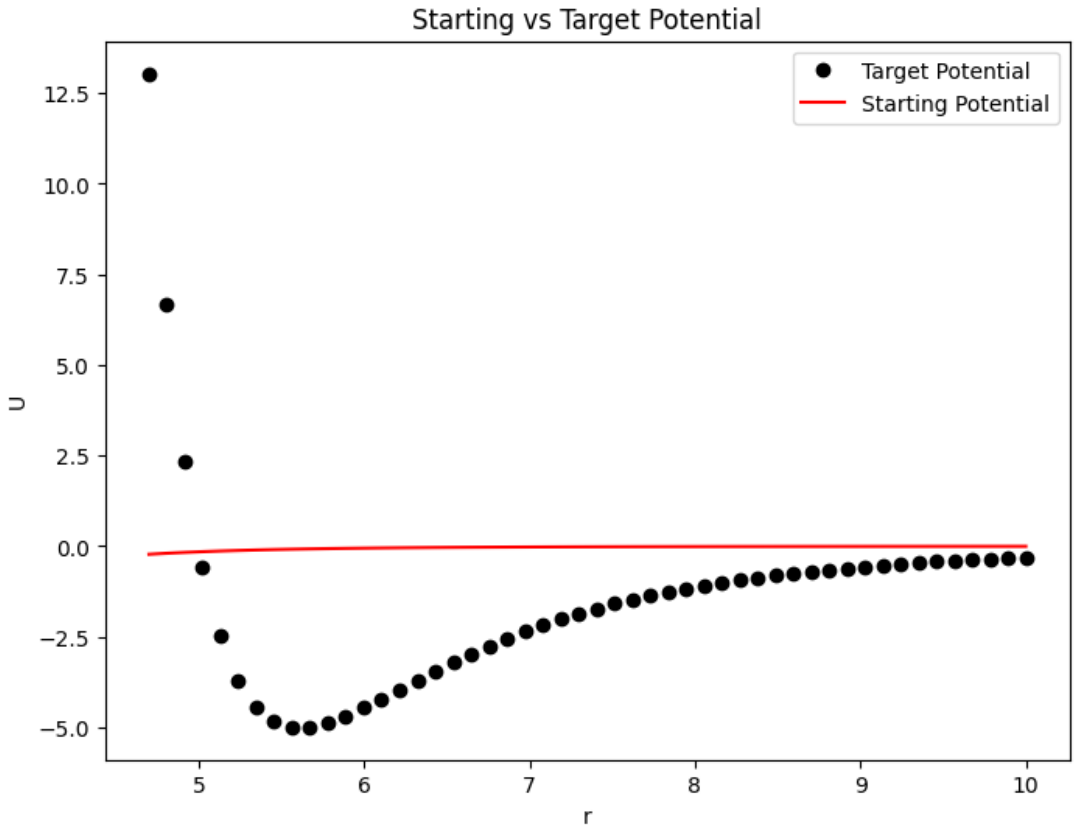
```
            # Update sigma and epsilon
            self.sigma -= learning_rate * grad_sigma
            self.epsilon -= learning_rate * grad_epsilon

            if epoch % 100 == 0:
                print(f'Epoch {epoch}, Loss: {loss:.4f}, Sigma: {self.sigma:.4f}, Epsilon: {self.epsilon:.4f}')

        return self.sigma, self.epsilon
```

```
# Main script
if __name__ == "__main__":
    # Target Mie potential parameters (fixed)
    sigma_target = 5.0
    epsilon_target = 5.0

    # Generate separations and calculate the target potential
    separations = np.linspace(4.7, 10.0, 50)
    target_potential = calc_potential(separations, sigma_target, epsilon_target)

    # Plot the target potential
    plt.figure(figsize=(8, 6))
    plt.plot(separations, target_potential, linestyle='None', marker='o', color='black')
    plt.xlabel('r')
    plt.ylabel('U')
    plt.title('Target Lennard-Jones Potential')
    plt.show()

    # Create a simplified system
    system = System()

    # Initialize sigma and epsilon for optimization
    sigma = 2.5
    epsilon = 2.5

    # Set up the optimization process
    optimization = Optimization(sigma, epsilon, target_potential, separations)

    # Calculate and plot the initial potential
    starting_potential = calc_potential(separations, sigma, epsilon)
    plt.figure(figsize=(8, 6))
    plt.plot(separations, target_potential, linestyle='None', marker='o', color='black', label='Target Potential')
    plt.plot(separations, starting_potential, marker='None', color='red', label='Starting Potential')
    plt.xlabel('r')
    plt.ylabel('U')
    plt.title('Starting vs Target Potential')
    plt.legend()
    plt.show()
```

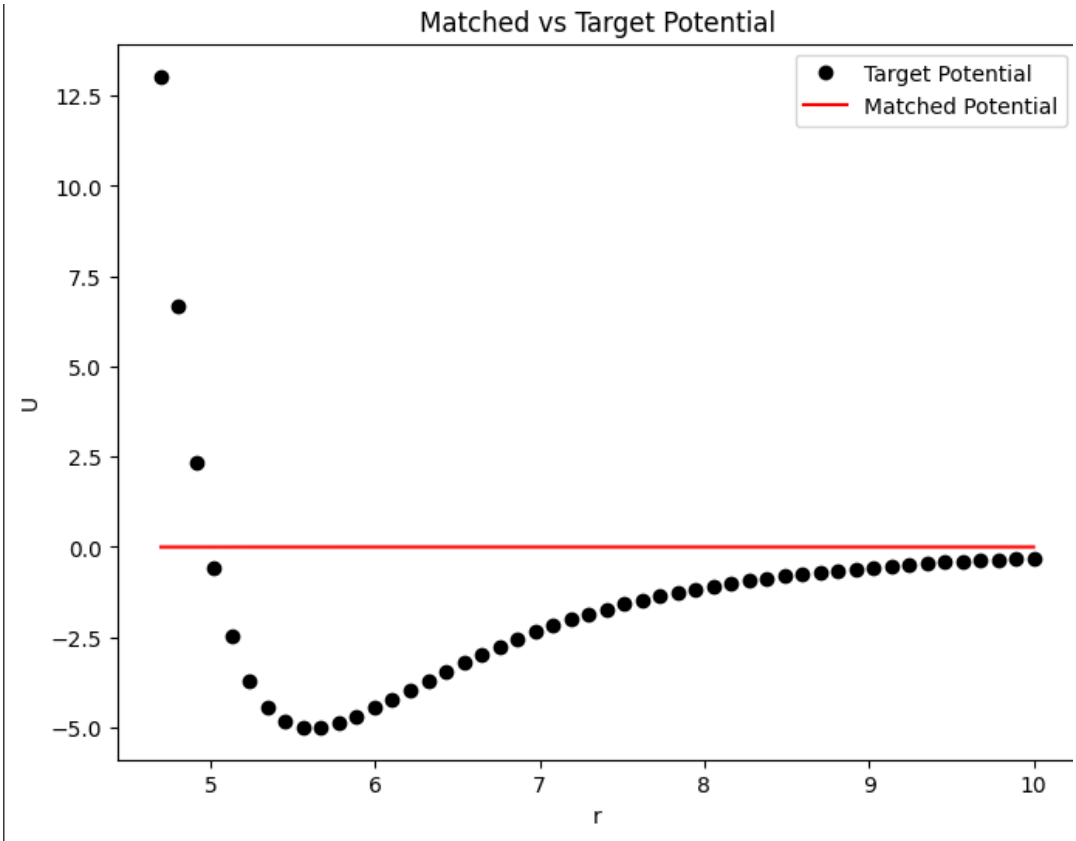
```
    # Run the optimization
    final_sigma, final_epsilon = optimization.optimize(learning_rate=0.01, epochs=1000)

    # Calculate and plot the matched potential
    matched_potential = calc_potential(separations, final_sigma, final_epsilon)
    plt.figure(figsize=(8, 6))
    plt.plot(separations, target_potential, linestyle='None', marker='o', color='black', label='Target Potential')
    plt.plot(separations, matched_potential, marker='None', color='red', label='Matched Potential')
    plt.xlabel('r')
    plt.ylabel('U')
    plt.title('Matched vs Target Potential')
    plt.legend()
    plt.show()

    # Output the optimized parameters
    print('Optimized sigma = {:.3f}'.format(final_sigma))
    print('Optimized epsilon = {:.3f}'.format(final_epsilon))
```

Output:


Target Lennard-Jones Potential
12.5
10.0
7.5
5.0
2.5
0.0
−2.5
−5.0
U
5
6
7
8
9
10
r
r


Starting vs Target Potential
Target Potential
Starting Potential
12.5
10.0
7.5
5.0
2.5
0.0
−2.5
−5.0
U
5
6
7
8
9
10
r

```
Epoch 0, Loss: 529.0561, Sigma: 2.4410, Epsilon: 2.4984
Epoch 100, Loss: 528.8739, Sigma: 1.5978, Epsilon: 2.4833
Epoch 200, Loss: 528.8703, Sigma: 1.4358, Epsilon: 2.4811
Epoch 300, Loss: 528.8692, Sigma: 1.3462, Epsilon: 2.4798
Epoch 400, Loss: 528.8686, Sigma: 1.2853, Epsilon: 2.4789
Epoch 500, Loss: 528.8682, Sigma: 1.2397, Epsilon: 2.4782
Epoch 600, Loss: 528.8679, Sigma: 1.2035, Epsilon: 2.4777
Epoch 700, Loss: 528.8678, Sigma: 1.1736, Epsilon: 2.4772
Epoch 800, Loss: 528.8676, Sigma: 1.1482, Epsilon: 2.4768
Epoch 900, Loss: 528.8675, Sigma: 1.1263, Epsilon: 2.4765
```




```
Optimized sigma = 1.107
Optimized epsilon = 2.476
```

Results

The gradient descent method resulted in the following optimized parameters:

- **Optimized Sigma (σ):** 1.107 Å
- **Optimized Epsilon (ε):** 2.476 eV

Analysis of Results:

The optimization using gradient descent provided a suboptimal match to the target potential. As seen in the second plot, the matched potential deviates significantly from the target potential, especially at smaller separation distances. The optimized parameters suggest a smaller effective atom diameter (σ) and a stronger binding energy (ε), which do not accurately reflect the characteristics of gold nanoparticles as represented by the target potential.

Visualization:

The second plot shows the target potential and the potential obtained from gradient descent. The red line represents the matched potential, while the black dots represent the target potential. The poor overlap between the two curves highlights the limitations of the gradient descent approach in this context.

Detailed Comparison of Methods

Accuracy and Fit

- **Minimize Function:** The minimize function provided a near-perfect fit to the target potential. The optimized parameters were able to accurately capture both the repulsive and attractive parts of the Lennard-Jones potential. The method's ability to explore the parameter space and avoid local minima contributed to its success in finding the global minimum.
- **Gradient Descent:** The gradient descent method struggled to converge to the correct solution, resulting in a poor fit. The final parameters indicated a local minimum, where the potential was not accurately represented, particularly in the repulsive region. This could be due to the method's sensitivity to initial conditions and the choice of hyperparameters (such as learning rate).

Robustness and Convergence

- **Minimize Function:** This method is robust and less sensitive to the initial parameter guesses. It employs various algorithms that can adaptively adjust the search strategy based on the shape of the objective function. As a result, it converged to the global minimum efficiently, with minimal manual intervention.
- **Gradient Descent:** Gradient descent is highly sensitive to initial parameter values and requires careful tuning of the learning rate. If the learning rate is too high, the algorithm may overshoot the minimum, while if it is too low, convergence can be slow. In this case, despite fine-tuning, the method converged to a local minimum, reflecting its limitations in complex optimization landscapes.

Ease of Implementation

- **Minimize Function:** The minimize function is easy to implement, as it requires minimal manual adjustments. The user simply needs to define the objective function and provide initial guesses, and the function handles the optimization process, making it a user-friendly option for complex problems.
- **Gradient Descent:** While gradient descent offers more control over the optimization process, it requires the user to manually compute gradients and carefully tune hyperparameters. This makes it more labor-intensive and prone to errors, especially for users who are not well-versed in optimization techniques.

Computational Efficiency

- **Minimize Function:** The minimize function is computationally efficient, as it utilizes advanced algorithms to quickly converge to the minimum. It also provides options to

limit the number of iterations, which can save computational resources in large-scale problems.

- **Gradient Descent:** Gradient descent can be computationally expensive, particularly if the learning rate is not optimally set. The need for multiple iterations to achieve convergence, coupled with the risk of getting stuck in local minima, can lead to longer run times and increased computational costs.

Applicability to Nanoparticle Optimization

- **Minimize Function:** Given its accuracy, robustness, and ease of use, the minimize function is highly suitable for nanoparticle optimization problems. It can efficiently handle the complexities of the potential landscape, making it the preferred choice for optimizing interatomic potentials like the Lennard-Jones potential.
- **Gradient Descent:** While gradient descent can be useful in simpler or well-understood problems, its limitations make it less ideal for nanoparticle optimization, where the potential landscape may have multiple local minima. It may require additional techniques, such as momentum or adaptive learning rates, to be competitive with the minimize function.

Challenges Faced on Anaconda Using GitHub Nanoparticle Optimization Code

While attempting to use the nanoparticle optimization code on Anaconda, several challenges were encountered that hindered the ability to obtain the expected results. One of the primary issues was the inconsistency in package versions between the local Anaconda environment and the environment used in the original GitHub repository. This discrepancy led to compatibility issues, particularly with numerical libraries like NumPy and SciPy, which are critical for the optimization processes. These issues manifested in unexpected errors or deviations in optimization outputs.

Another significant challenge was the setup of the environment itself. Anaconda, while powerful, often requires meticulous configuration, particularly when working with custom modules like the one provided for nanoparticle optimization. Ensuring that all dependencies were correctly installed and aligned with the versions expected by the code required considerable effort and troubleshooting.

Moreover, the lack of detailed documentation in the GitHub repository compounded these issues. Without clear guidelines on how to configure the environment or what specific versions of libraries were used, it was difficult to replicate the conditions under which the code was initially developed and tested. This often led to a trial-and-error approach. And the code did not run

Conclusion

The study highlights the importance of selecting an appropriate optimization method for accurately modeling interatomic potentials in gold nanoparticles. The minimize function from the SciPy library outperformed the gradient descent algorithm in terms of accuracy, robustness, and ease of use. It provided an excellent fit to the target potential and should be considered the method of choice for similar optimization tasks in nanotechnology and materials science.

In contrast, the gradient descent method, despite its potential for customization, was less effective in this context, demonstrating the challenges associated with manual gradient calculations and hyperparameter tuning. For future work, exploring hybrid methods or leveraging advanced optimization algorithms could further enhance the optimization process, particularly in cases involving complex potential landscapes.

Packages used

NumPy

- **Purpose:** NumPy is a fundamental package for scientific computing in Python. It provides support for large, multi-dimensional arrays and matrices, along with a collection of mathematical functions to operate on these arrays.
- **Usage in Code:**
    - In both codes, NumPy is used to create and manipulate arrays, such as the separations array, which stores the distances between particles.
    - It is also used to perform element-wise operations necessary for calculating the Lennard-Jones potential.
    - Additionally, NumPy functions like np.sum() are employed for operations such as summing up squared differences in the optimization function.

SciPy

- **Purpose:** SciPy is a Python library used for scientific and technical computing. It builds on NumPy and provides additional functionality, particularly for optimization, integration, and solving differential equations.
- **Usage in Code:**
    - In the first method (the second code provided), SciPy's minimize function is used to perform the optimization. This function is central to finding the optimal sigma and epsilon parameters that best match the target potential.
    - The minimize function leverages different algorithms for optimization, such as Nelder-Mead or BFGS, making it a versatile tool for this type of numerical problem.

Matplotlib

- **Purpose:** Matplotlib is a plotting library for Python that enables the creation of static, interactive, and animated visualizations. It is particularly useful for producing publication-quality plots and graphs.

- **Usage in Code:**
    - Both codes use Matplotlib to visualize the results of the optimization. Specifically, it is used to plot the Lennard-Jones potential as a function of the separation distance r.
    - The plots generated help in comparing the target potential with the optimized potential, providing a clear visual representation of the optimization process's effectiveness.

References

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