12-623/24-623 2016 HW#1 Solutions

1. (20 points) Download the program start.cpp and the file 5input.txt from Blackboard. This program shows examples of input/output and data structures. If you are not familiar with programming, spend some time figuring out what this program does and how it works.

Modify start.cpp so that it:

(i) Evaluates the polynomial $2x^6 - 3x^4 + 4x^2 - 3$ using both "int" and "double" variables. In your submission, describe the most computationally efficient way to evaluate this function.

(ii) Determines if the integer is prime. In your submission, explain how your algorithm works.

Run the program for the following set of integers: (11, 28, 45, 397, 677, 951, 2552, 6447, 6449, 7411, 7412). Compare and explain what happens when you evaluate the polynomial using "int" or "double" variables. Submit your output and a discussion of any issues related to the results that might be of interest.

Solution

A copy of the modified program, called prime.cpp, is on Blackboard.

(ii) Whenever you write a program, you want it to run as fast as possible. To do this, you need to have some idea about how the computer performs calculations. For example, it is faster to evaluate $x \times x$ than to evaluate x^2. For the given function, $2x^6 - 3x^4 + 4x^2 - 3$, the naive implementation in C++ would be:

```
f = 2.*pow(x,6) - 3.*pow(x,4) + 4*pow(x,2) - 3.;
```

A better evaluation is:

```
f = 2.*x*x*x*x*x*x - 3.*x*x*x*x + 4.*x*x - 3.;
```

which uses 12 multiplications. An even better way is to declare an intermediate quantity:

```
x2 = x*x;
f = 2.*x2*x2*x2 - 3.*x2*x2 + 4*x2 -3;
```

which uses 7 multiplications. Even better,

```
x2 = x*x;
x4 = x2*x2;
f = 2.*x4*x2 - 3.*x4 + 4.*x2 -3.;
```

which uses 6 multiplications.

(iii) There are many ways to check if a number is prime. Efficient algorithms have been developed to work with very large numbers. The given solutions implements a very simple scheme, where the number in question is divided by integers starting at 2, and the remainder is checked. If the remainder is zero, the number is not prime, and the loop terminates. A check in the program is included in case someone tries to slip in zero or a negative number.

When evaluating the function f using integers, the following results are obtained:

The number 11 is not a perfect square, prime, and returns a value of 3499680 when inserted into the function f
The number 28 is not a perfect square, not prime, and returns a value of 961939773 when inserted into the function f
The number 45 is not a perfect square, not prime, and returns a value of -584631712 when inserted into the function f
The number 397 is not a perfect square, prime, and returns a value of -361058976 when inserted into the function f
The number 677 is not a perfect square, prime, and returns a value of -402784224 when inserted into the function f
The number 951 is not a perfect square, not prime, and returns a value of -129610176 when inserted into the function f
The number 2552 is not a perfect square, not prime, and returns a value of -2071637763 when inserted into the function f
The number 6447 is not a perfect square, not prime, and returns a value of 879593088 when inserted into the function f
The number 6449 is not a perfect square, prime, and returns a value of 1282775424 when inserted into the function f
The number 7411 is not a perfect square, prime, and returns a value of 1689934176 when inserted into the function f
The number 7412 is not a perfect square, not prime, and returns a value of 1747996477 when inserted into the function f

The function values are clearly not correct other than for 11 and 28. $7412^6 \sim 1.66 \times 10^{23}$, and not a number on the order of 10^9! What has happened is that we have exceeded the size of the memory allotted to the "integer" variable, and the answer returns nonsense. As an alternative, we can evaluate the function using double precision numbers, which leads to the following results:

The number 11 is not a perfect square, prime, and returns a value of 3.49968e+006 when inserted into the function f
The number 28 is not a perfect square, not prime, and returns a value of 9.6194e+008 when inserted into the function f
The number 45 is not a perfect square, not prime, and returns a value of 1.65952e+010 when inserted into the function f
The number 397 is not a perfect square, prime, and returns a value of 7.83013e+015 when inserted into the function f
The number 677 is not a perfect square, prime, and returns a value of 1.92558e+017 when inserted into the function f
The number 951 is not a perfect square, not prime, and returns a value of 1.47949e+018 when inserted into the function f

The number 2552 is not a perfect square, not prime, and returns a value of 5.52477e+020 when inserted into the function f
The number 6447 is not a perfect square, not prime, and returns a value of 1.43607e+023 when inserted into the function f
The number 6449 is not a perfect square, prime, and returns a value of 1.43875e+023 when inserted into the function f
The number 7411 is not a perfect square, prime, and returns a value of 3.31353e+023 when inserted into the function f
The number 7412 is not a perfect square, not prime, and returns a value of 3.31621e+023 when inserted into the function f

While there is a loss of accuracy, we get reasonable results. When doing calculation in a program, it is important to keep these kinds of things in mind.

2. (9 points) Find two papers in the scientific literature of interest to you that use either molecular dynamics or Monte Carlo simulations. Include these papers in your submission. Write one page explaining why you chose these papers.

3. (6 points total)

(a) (3 points) Calculate how many water molecules are in spherical droplets with diameters of 1 nm, 10 nm, and 100 nm.

(b) (3 points) Assume that you will treat each water molecule as three point masses that are rigidly connected. How many distinct pair interactions are there in each of the droplets from (a)?

Solution

(a) If the droplet diameter is d, then its volume $V_{droplet}$ is $\pi d^3/6$. The mass of one water molecule, $m_{\mathrm{H_2O}}$, is 18 $\times$ (atomic mass unit) $= 18 \times 1.6605 \times 10^{-27}$ kg$= 2.98897 \times 10^{-26}$ kg. Take the density of bulk water to be $\rho = 1000$ kg/m^3. The volume taken up by one molecule is therefore

$$V_{\mathrm{H_2O}} = \frac{m_{\mathrm{H_2O}}}{\rho} = \frac{2.98897 \times 10^{-26}\mathrm{kg}}{1000\mathrm{kg/m}^3} = 2.98897 \times 10^{-29}\mathrm{m}^3.$$

The number of water molecules in a droplet of diameter d is therefore

$$N = \frac{V_{droplet}}{V_{\mathrm{H_2O}}}$$

Note that the expression for N can give a non-integer value. The results below correspond to floor(N).

For $d = 1$ nm, $N = 17$.
For $d = 10$ nm, $N = 17,517$.
For $d = 100$ nm, $N = 17,517,699$.

(b) If there are N water molecules, there are $N(N-1)$ pairs of molecules. Removing double counting, there are $N(N-1)/2$ distinct pairs. If there are three rigid masses on each water molecule (that don't interact with one another), then each distinct pair of water molecules has nine interactions associated with it, leading to $9N(N-1)/2)$ distinct pair interactions.

For $N = 17$, 1224 interaction.
For $N = 17,517$, 1,380,724,974 interactions.
For $N = 17,517,699$, 1,380,913,923,316,059 interactions. This number is big.

4. (15 points total) The Lennard-Jones (LJ) potential is given by

$$u(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right], \tag{1}$$

where ϵ and σ are the energy scale and the length scale. The LJ mass scale is m, the mass of one atom. Equation (1) describes how two isolated atoms interact. It does not describe the environment experienced by an atom in a crystal. The energy of an atom i in a crystal can be found by summing over the contributions of all other atoms:

$$U_i = \frac{1}{2} \sum_{j \neq i} u(r_{ij}). \tag{2}$$

The stable crystal structure of LJ solids is face-centered cubic (fcc). In this case, Eq. (**??**) can be written as a function of the nearest neighbor distance, r_{nn}, as

$$U_i(r_{nn}) = 2\epsilon \left[A_{12} \left(\frac{\sigma}{r_{nn}} \right)^{12} - A_6 \left(\frac{\sigma}{r_{nn}} \right)^{6} \right], \tag{3}$$

where $A_{12} = 12.13$ and $A_6 = 14.45$.

(a) (5 points) Show Eqs. (1) and (3) together on a plot of (u or U_i)/ϵ vs. (r or r_{nn})/σ. Based on the shapes of the two curves, describe how the environment experienced by an atom in each will be different.

(b) (4 points) Analytically determine the value of r (or r_{nn}) at which the energy is zero and at which the energy is a minimum for each of Eqs. (1) and (3) in terms of the LJ scales. Show these points on the plot from part (a).

(c) (2 points) Determine the LJ thermal conductivity scale [i.e., the combination of the mass, energy, and length scales, and the Boltzmann constant (k_B) that gives units of W/m-K].

(d) (4 points) A molecular dynamics simulation for LJ argon run at a temperature of 20 K predicts a thermal conductivity of 1.4 W/m-K. Determine the dimensionless temperature and dimensionless thermal conductivity corresponding to this simulation. What are the corresponding temperature and thermal conductivity for LJ krypton based on these dimensionless values?

For argon: $\epsilon = 1.67 \times 10^{-21}$ J, $\sigma = 3.40 \times 10^{-10}$ m, and $m = 6.63 \times 10^{-26}$ kg.
For krypton: $\epsilon = 2.24 \times 10^{-21}$ J, $\sigma = 3.65 \times 10^{-10}$ m, and $m = 13.9 \times 10^{-26}$ kg.
$k_\mathrm{B} = 1.3806 \times 10^{-23}$ J/K.

Solution

(a) See the attached plot. The well of the effective potential is deeper than that of the pair potential. The force on an atom is related to the slope of the potential. Thus, atoms in the effective potential will have stronger forces acting on them if they move away from their equilibrium position. From an energetic standpoint, it requires less energy to separate two atoms in free space than it does to remove an atom from a solid.

(b) For the pair potential, the energy is zero when

$$r(u=0) = \sigma = 3.4\text{Å}.$$

The energy is minimum when

$$\frac{\partial u}{\partial r} = 0,$$

which leads to

$$r(u_{min}) = 2^{1/6}\sigma = 3.816\text{Å}.$$

Repeating for the effective potential,

$$\begin{aligned}
r_{nn}(U_i = 0) &= \left(\frac{A_{12}}{A_6}\right)^{1/6}\sigma = 0.97125\sigma = 3.302\text{Å} \\
r_{nn}(U_{i,min}) &= \left(\frac{2A_{12}}{A_6}\right)^{1/6}\sigma = 1.09019\sigma = 3.712\text{Å}.
\end{aligned}$$

These four points are shown in the plot from part (a) with the labels a-d.

(c) The Lennard-Jones thermal conductivity scale is

$$\frac{k_\mathrm{B}}{\sigma^2}\left(\frac{\epsilon}{m}\right)^{1/2}.$$

(d) For LJ, the temperature scale is ϵ/k_B and the thermal conductivity scale was found in (c).

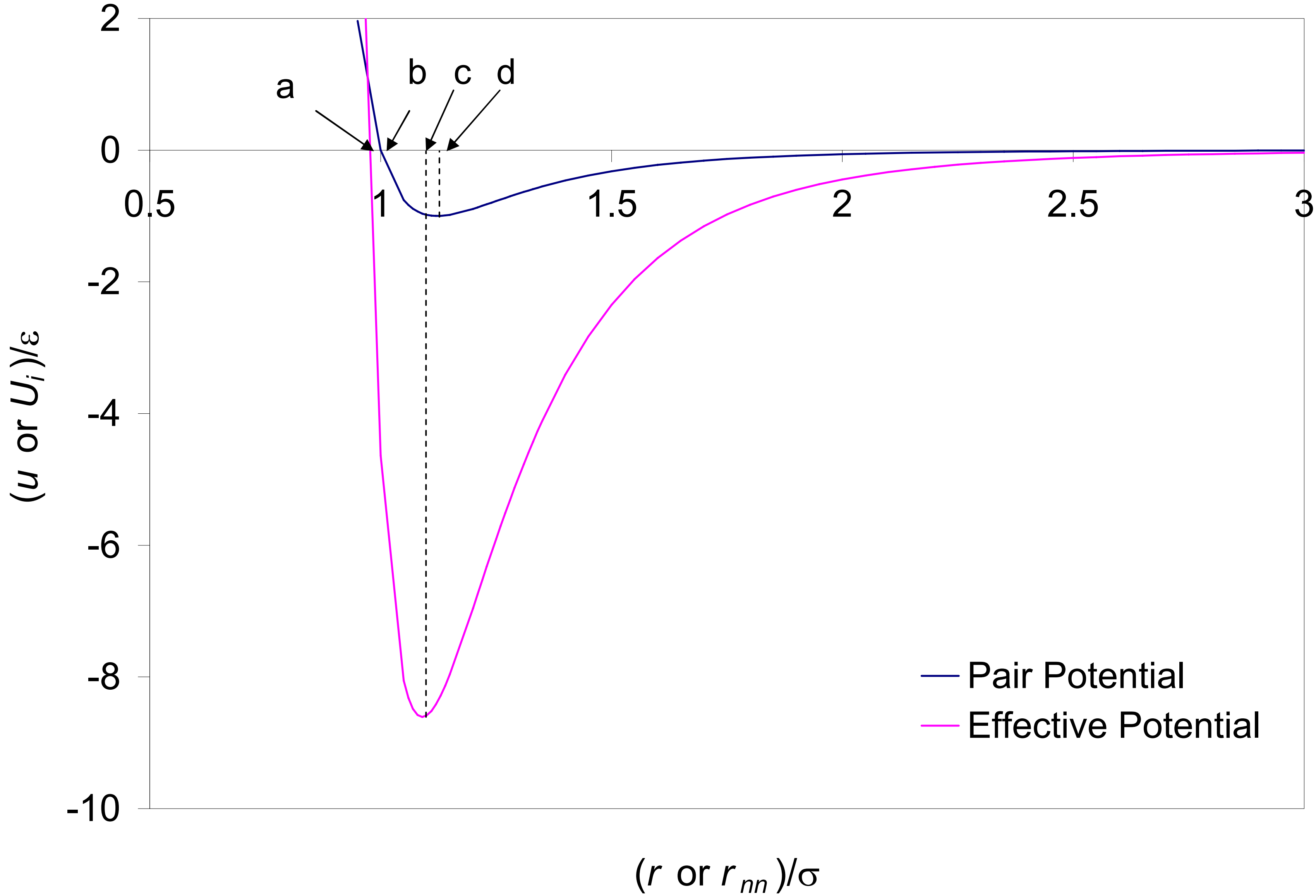
For argon, the scales are

$$\begin{aligned}
T_{Ar} &= \left(\frac{\epsilon}{k_\mathrm{B}}\right)_{Ar} = \frac{1.67\times10^{-21}\mathrm{J}}{1.3806\times10^{-23}\mathrm{J}/K} = 121 \text{ K}. \\
k_{Ar} &= \left[\frac{k_\mathrm{B}}{\sigma_\mathrm{LJ}^2}\left(\frac{\epsilon_\mathrm{LJ}}{m_\mathrm{LJ}}\right)^{1/2}\right]_{Ar} = \frac{1.3806\times10^{-23}\mathrm{J}/K}{(3.40\times10^{-10}\text{ m})^2}\left(\frac{1.67\times10^{-21}\mathrm{J}}{6.63\times10^{-26}\text{ kg}}\right)^{1/2} = 0.0190 \text{ W/m-K}.
\end{aligned}$$

For krypton, the scales are

$$\begin{aligned}
T_{Kr} &= \left(\frac{\epsilon}{k_\mathrm{B}}\right)_{Kr} = \frac{2.24\times10^{-21}\mathrm{J}}{1.3806\times10^{-23}\mathrm{J}/K} = 162 \text{ K}. \\
k_{Kr} &= \left[\frac{k_\mathrm{B}}{\sigma_\mathrm{LJ}^2}\left(\frac{\epsilon_\mathrm{LJ}}{m_\mathrm{LJ}}\right)^{1/2}\right]_{Kr} = \frac{1.3806\times10^{-23}\mathrm{J}/K}{(3.65\times10^{-10}\text{ m})^2}\left(\frac{2.24\times10^{-21}\mathrm{J}}{13.9\times10^{-26}\text{ kg}}\right)^{1/2} = 0.0132 \text{ W/m-K}.
\end{aligned}$$

The dimensionless temperature is (20 K)/(121 K) = 0.165.
The dimensionless thermal conductivity is (1.4 W/m-K)/(0.0190 W/m-K) = 73.9.
The krypton temperature is (0.165)(162 K) = 26.8 K.
The krypton thermal conductivity is (73.9)(0.0132) = 0.972 W/m-K.


2
0
-2
-4
-6
-8
-10
0.5
1
1.5
2
2.5
3
a
b
c
d
(u or U_i)/ε
(r or r_nn)/σ
Pair Potential
Effective Potential