24-623 2015 HM4

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1 Problem 1

The regular equations for the velocity verlet scheme are as follows:

1. $v_i(t + \Delta t/2) = v_i(t) + F_i(t)\Delta t/2m_i$
2. $r_i(t + \Delta t) = r_i(t) + v_i(t + \Delta t/2)\Delta t$
3. $v_i(t + \Delta t) = v_i(t + \Delta t) + F_i(t + \Delta t)\Delta t/2m_i$

With MD simulations in NVT ensemble using the Nose-Hoover thermostat, the following are the equations of motions,

1. $\dot{r_i} = \mathbf{v_i}$
2. $\dot{\mathbf{v}}_\mathbf{i} = \mathbf{F_i}/m_i - \eta\mathbf{v_i}$
3. $\eta = \frac{1}{\tau_T^2}\left(\frac{T}{T_{set}} - 1\right)$

Now replacing the acceleration term with the above equations of motion.

$$v_i(t + \Delta t/2) = v_i(t) + (\mathbf{F_i(t)}/\mathbf{m_i})\Delta t/2 \tag{1}$$

$$F_i(t)/m_i = a_i \implies \dot{\mathbf{v}}_\mathbf{i} = \mathbf{F_i}/m_i - \eta\mathbf{v_i} \tag{2}$$

Now substitute the above equation in original Step 3,

$$\boxed{v_i(t + \Delta t/2) = v_i(t) + [\mathbf{F_i}/m_i - \eta(t)\mathbf{v_i(t)}]\Delta/2} \tag{3}$$

The Step 2 for the evolution of position remains the same as the actual expression.
The Step 3 is driven by the $F_i(t + \Delta t)/m_i$, which is the acceleration at $(t + \Delta t)$

$$v_i(t + \Delta t) = v_i(t + \Delta t/2) + F_i(t + \Delta t)\Delta t/2m_i \tag{4}$$

If we replace the force term at $(t + \Delta t)$ from the Step 3 with the modified equations of motions as follows,

$$\dot{\mathbf{v}}_\mathbf{i}(t + \Delta t) = \mathbf{F_i}(\mathbf{t} + \mathbf{\Delta t})/m_i - \eta(t + \Delta t)\mathbf{v_i}(\mathbf{t} + \mathbf{\Delta t}) \tag{5}$$

Substitute the above expression in 4, would give

$$v_i(t + \Delta t) = v_i(t + \Delta t) + [\mathbf{F_i}(\mathbf{t} + \mathbf{\Delta t})/m_i - \eta(t + \Delta t)\mathbf{v_i}(\mathbf{t} + \mathbf{\Delta t})]\Delta t/2 \tag{6}$$

Rearranging the expression results in,

$$v_i(t + \Delta t) = v_i(t + \Delta t) + F_i(t + \Delta t)\Delta t/(2m_i) - v_i(t + \Delta t)\eta(t + \Delta t)\Delta t/2 \tag{7}$$

$$v_i(t+\Delta t)\Big(1+\eta(t+\Delta t)\Delta t/2\Big) = v_i(t+\Delta t) + F_i(t+\Delta t)\Delta t/(2m_i) \tag{8}$$

$$\boxed{\mathbf{v}_i(t+\Delta t) = \frac{\mathbf{v}_i(t+\Delta t) + \mathbf{F}_i(t+\Delta t)\Delta/(2m_i)}{1+\eta(t+\Delta t)\Delta t/2}} \tag{9}$$

Note that the $\eta(t+\Delta t)$ is obtained from the modified equation of motion using simple forward difference rule:

$$\dot{\eta} = \frac{d\eta}{dt} = \frac{1}{\tau_T^2}\Big(\frac{T}{T_{set}} - 1\Big) \tag{10}$$

$$\frac{\eta(t+\Delta t) - \eta(t)}{\Delta t} = \frac{1}{\tau_T^2}\Big(\frac{T}{T_{set}} - 1\Big) \tag{11}$$

$$\boxed{\eta(t+\Delta t) = \eta(t) + \frac{\Delta t}{\tau_T^2}\Big(\frac{T}{T_{set}} - 1\Big)} \tag{12}$$

2 Problem 2

2.1 a)

Average Pressure is plotted as the function of density between 950 kg/m^3 and 1150 kg/m^3. A trendline is fit and the zero pressure density is found to be at 1042.8 kg/m^3 which slightly varies with the density computed from the previous computations corresponding to 1053.8 kg/m^3.

1. Several NVT simulations are performed with NVT ensemble and Nose-Hoover thermostat and ensuring temperature of 100K is reached for every run.

2. Equlibration is completed, as judged by the lack of energy drift in the 200 units of MD simulation. $\big\langle (E - \langle E\rangle)\big\rangle$ per atom is in the order of 1e-3 which indicate the energy fluctuations are very small.

Plots of energies, temeprature and pressure are shown below for a configuration approaching zero pressure NVT simulation for 200 LJ units. Plots for all other configurations can be found in the submission file. The plots are shown in Figs.1, 2, 3 respectively.

Plot of average pressure in non-dimensional units is plotted against the density and a trendline is fit as shown below in Fig.4

2.2 b)

To compute the heat capacity of argon, the following expression is being used,

$$\langle T\rangle = \Big[\frac{\big\langle (E - \langle E\rangle)^2\big\rangle}{3(N-1)k_B c_v}\Big]^{1/2} \tag{13}$$

From the above equation, c_v is the heat capacity per atom at constant volume. As there are N atoms, the heat capacity of the system is given by :

$$C_{v,system} = \frac{\big\langle (E - \langle E\rangle)^2\big\rangle}{k_B \langle T\rangle^2} \tag{14}$$

where k_B is boltzmann constant = 1.3806488e-23 J/K and the $\langle T\rangle = 100K$. Energy from the simulation has to be converted from LJ units to SI units using $\epsilon = 1.67e-21J$.

For computing the heat capacity of the system, the lattice dimensions are found from the zero pressure density from the Fig.4. Using the density, volume is found and subsequently lattice length is found to be 7.47. Sufficiently long simulation is carried out such that the $\langle T\rangle = 100K$ as can be seen from the Fig:6. It

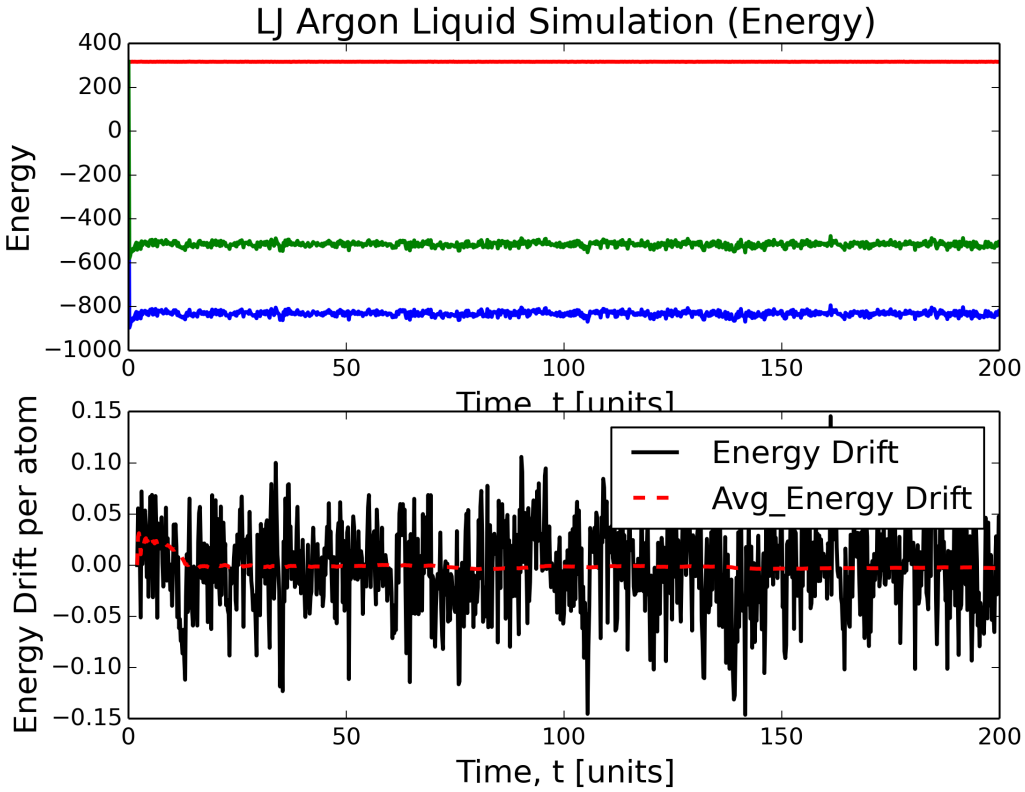

Figure 1: The figure shows the time evolution of energy and energy drift showing the equilibration of the system

is striking to see the average temperature(Fig.6), pressure(Fig.7) and the energy drift(Fig.5) converges well from all fluctuations.

After finding the mean of energy fluctuations, heat capacity of the system at constant volume is found to be:

$$C_{v,system} = \frac{255.29954 \times (1.67e-21)^2(J^2)}{1.3806488e-23(J/K) \times 100^2(K^2)} \tag{15}$$

Heat capacity is in the units of J/K and it is converted to J/Kg-K by using mass of 256 particles. The specific heat of the argon is found to be 303.8409 J/Kg-k.

3 Problem 3

3.1 a) Objectives

1. The objectives are very clear to predict the EACs between noble gases and graphite surfaces of different curvature.

2. Non-equilibrium steady-state simulations were helpful in exploring wide phase space and is insensitive to the initial conditions set.

3. Relating thermal boundary conductances between noble gases and graphene to EACs.

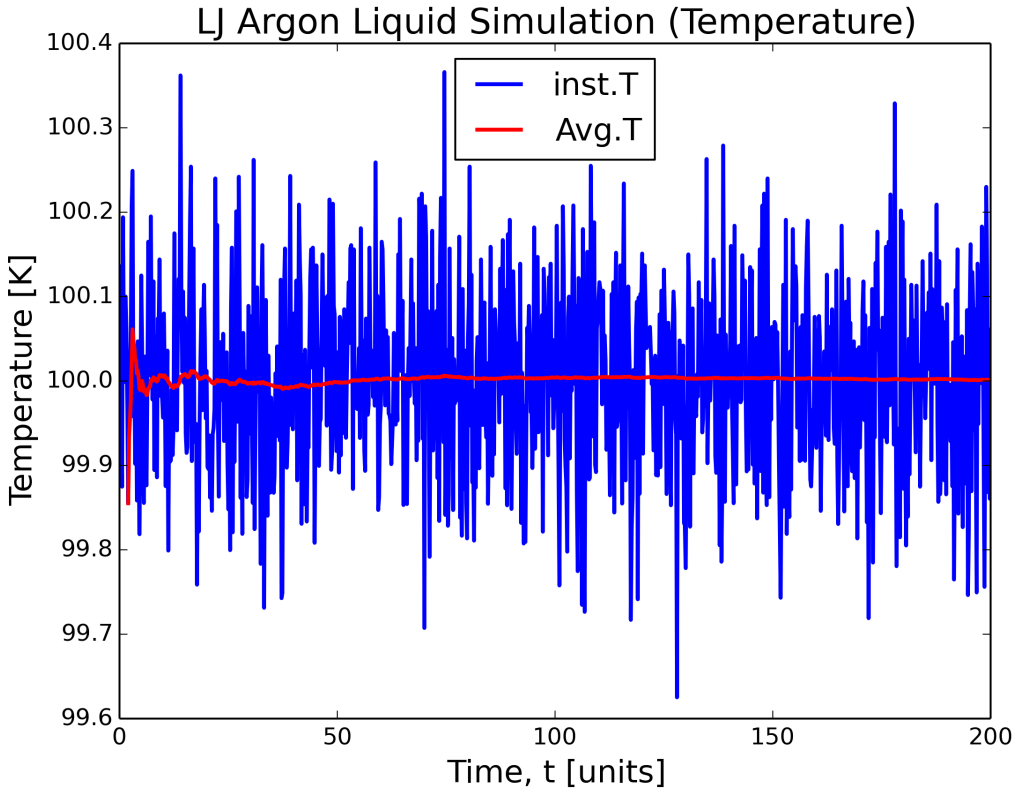

Figure 2: The figure shows the time evolution of temeprature and the equilibration of average temperature to 100K.

3.2 b) Conclusions

1. EAC increases with the increase in atomic mass of the noble gas and this can be attributed to heavier atoms having lower velocity resulting in longer interaction time with the CNT.

2. Layer-independence with respect to EAC is an interesting observation.

3. The profile of potential energy with respect to the gas atom distance from the CNT is predictable as it is goverened by Lennard Jones Potential but it is an interesting observation to find the depth of the gas-CNT potential increases with increase in CNT diameter.

4. As the potential depth increases, the interaction between gas and CNT is strong contributing to increase in EAC.

3.3 c) Concerns

1. In the MD simulations, global thermostate is turned-off and velocity-rescaling(VR) thermostat is used to control the temperatures at the source and sink. As VR thermostat doesn't really give NVT statistics there will be fluctuations in total energy. As the entire simulation seems to be in NVT ensemble, it is not clear how comparable are the energy drift, before and after equilibration with respect to the energy accomodation coefficient.

2. Can Nose-Hoover thermostat be used for velocity-rescaling to maintain heat source and sink.

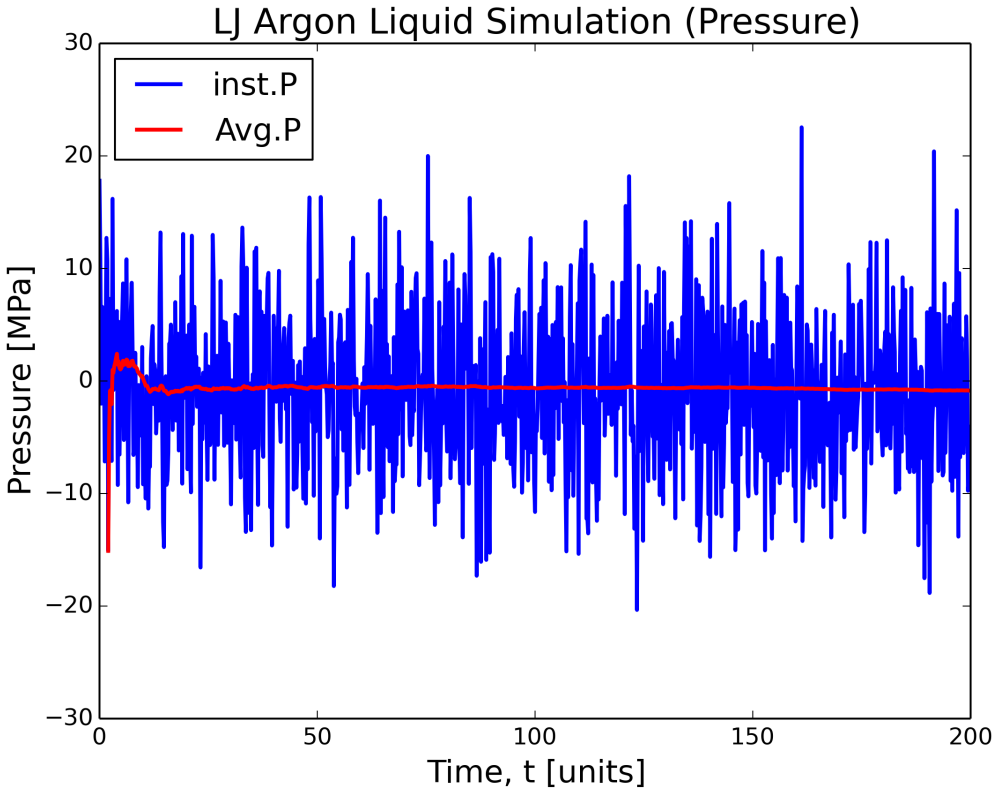

Figure 3: The figure shows the time evolution of Pressure and its closest approach to zero pressure.

3.4 d) Review

1. It is very important to note that the layer-independence EAC will likely not hold true for higher translational energy gas atoms and has been identified with relevant explanation.

2. It would have been much more supporting, if the information is provided for the EAC independence to multi-layer CNT.

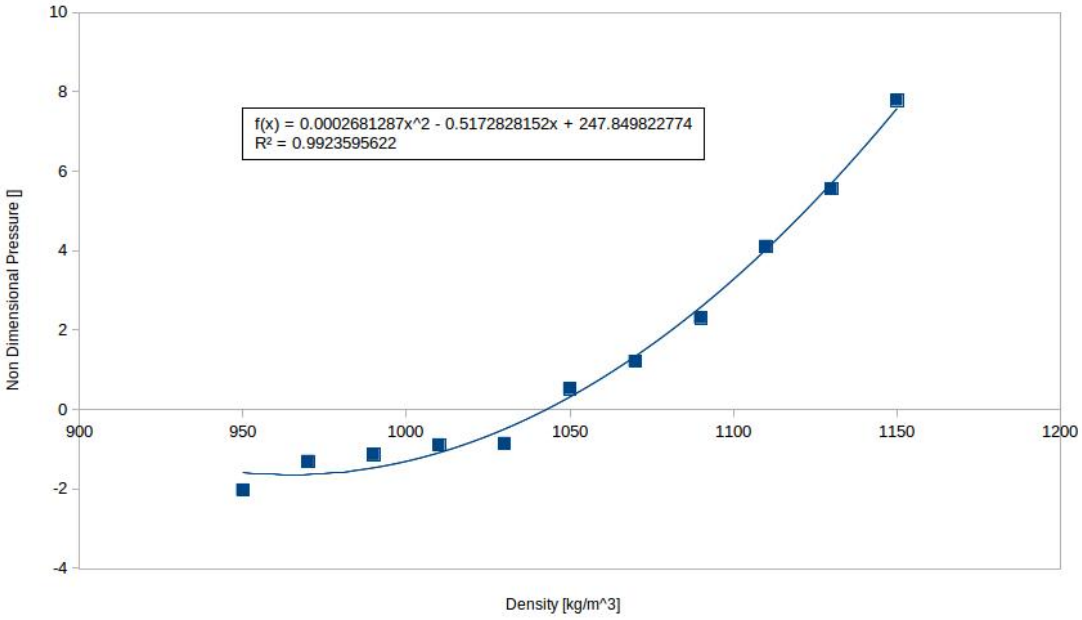

Figure 4: The figure shows the plot of average pressure as a function of density.

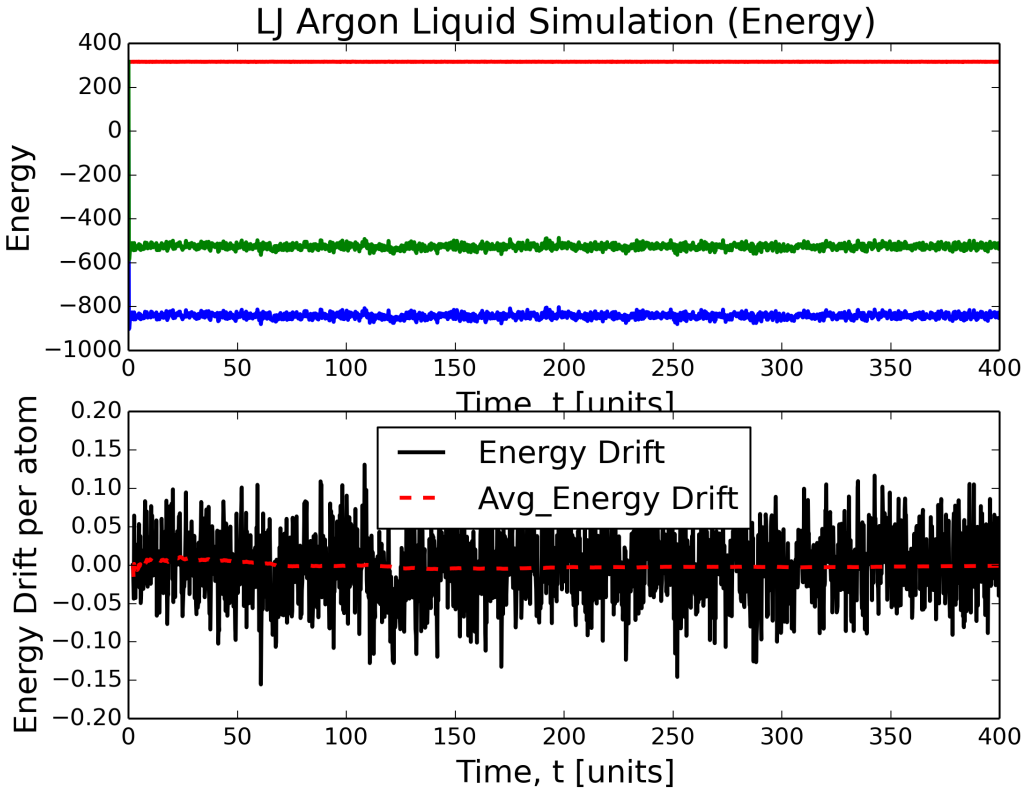

Figure 5: The figure shows the plot of time variation of energy over 400 units

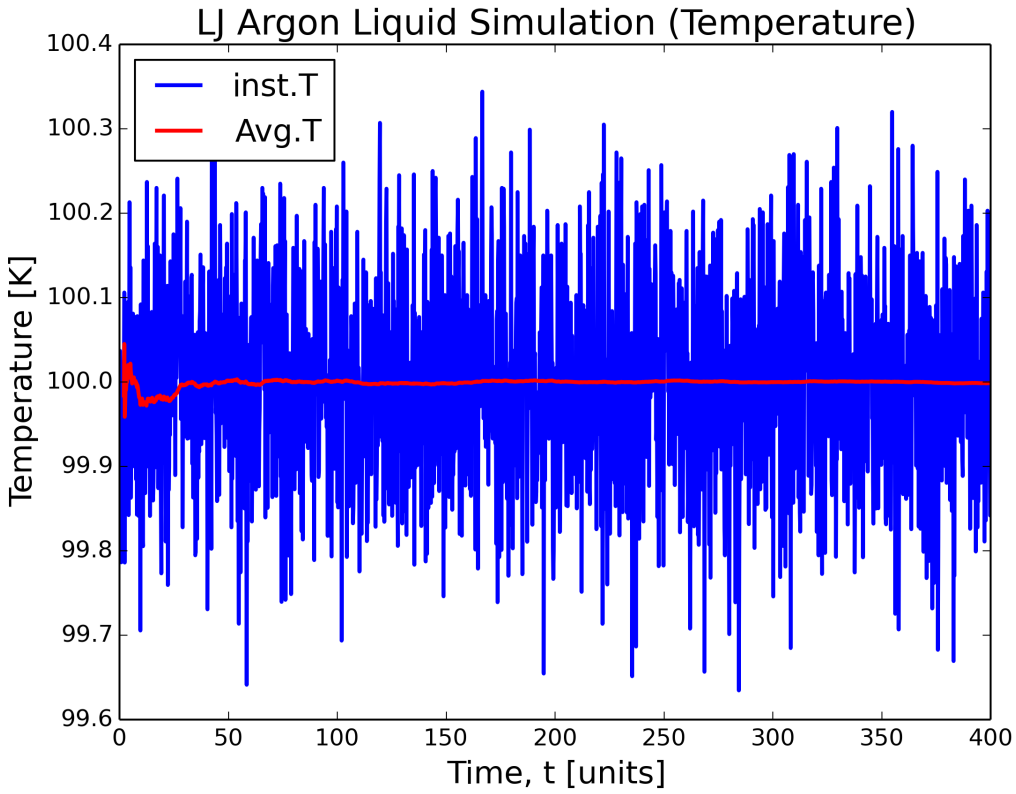

Figure 6: The figure shows the plot of average temperature approaching 100K on the time scale of 400 units

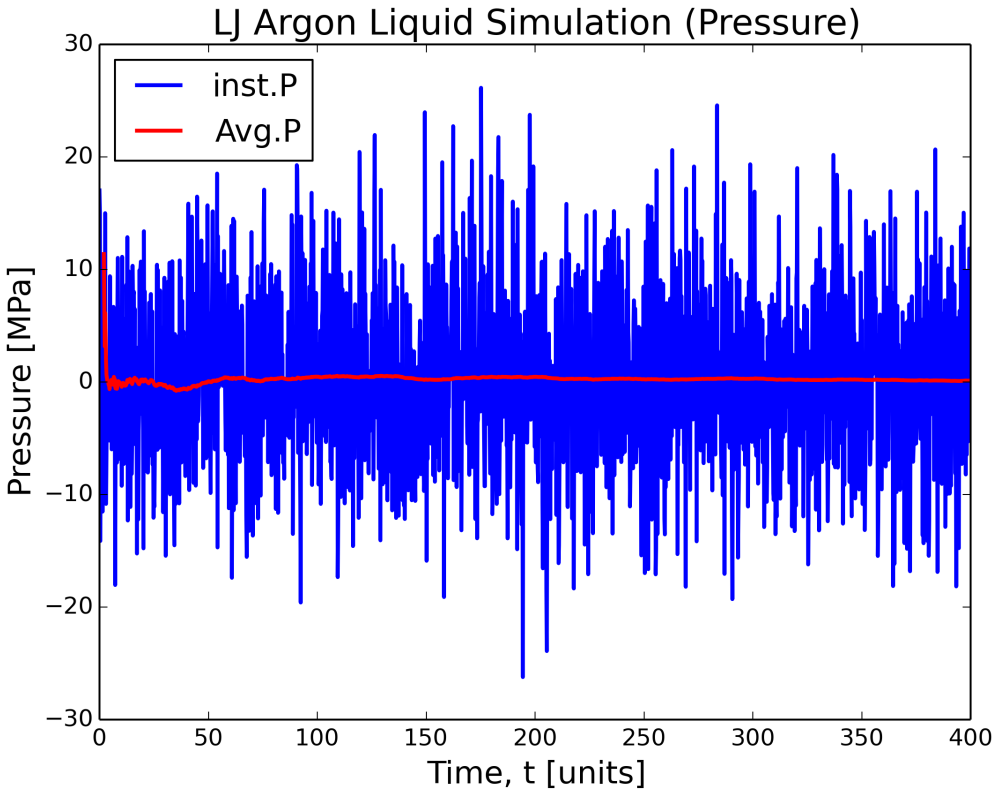

Figure 7: The figure shows the confirmation of zero pressure density for 400 units