Tim Keller
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Liquid-Vapor Interface of a Lennard-Jones System

Abstract:

A three dimensional molecular dynamics simulation was performed for a simple Lennard-Jones system to study a liquid-vapor interface. A clear separation can be seen between the two phases and with the density of the liquid and gas being approximately 5 and 0.8, respectively, in reduced units. During the production run the location of the liquid on the z-axis was not entirely stable, which may imply that the system hasn't completely reached equilibrium at the start of the production run or that more particles are needed to obtain good statistics.

Background:

Interfacial properties are very important for a wide range of biological and industrial applications. For example, the concentrations of ions and molecules are not necessarily homogeneous throughout a solution and can have a tendency to concentrate at the liquid-vapor interface or at the surface of a membrane. Additionally, the interface of oil mixtures is important for understanding the changes in viscosity when gases such as CO_2 are pumped into oil wells during tertiary oil recovery. Experimental difficulties exist in looking at surface phenomenon, mainly due to the size of the interface being quite small in comparison to the volume of bulk solution. It has been shown that simulation practices such as mean-field theory offer a good qualitative description of the mixture interface.[1] This work takes a simple Lennard-Jones system and attempts to extract the properties of a liquid-vapor interface

Methods:

The simulation was a three-dimensional molecular dynamics simulation using a Lennard-Jones 12-6 potential with parameters ϵ and σ given by Mecke et al.[1] The values of ϵ/k and σ were 117.05K and 0.33967nm, respectively. The variables were made dimensionless by defining the reduced temperature $T^* = kT/\epsilon$, the reduced length $z^* = z/\sigma$, and the reduced density as $\rho^* = \rho\sigma^3$. The temperature of the simulation was the same as Meche et al.[1], 115.77K.

The dimensions of the simulation box were $z = 3x = 3y$ and the simulation was performed with boundary conditions in all three dimensions. A cutoff distance of 3 was chosen.

Initially, the system was created with densities slightly greater than normal liquid densities in a cube of dimensions $x = y = z$. After equilibration, two additional cubes of identical dimensions were added to both sides of the cube in the z dimension. The vapor phase was allowed to form in the new system with $z = 3x = 3y$ and after equilibration the production run was started.

The density at each length was calculated by cutting the z - axis into 300 bins and averaging the number of particles in each bin over the production period.

Table 1: System parameters for MD simulation

Number of Particles	Box dimension x^* by z^*	Cube Init. Density	Cube Init. steps	Equil. steps	Prod. steps
540	9.1595 by 27.4785	0.7041	100000	100000	250000

Data:

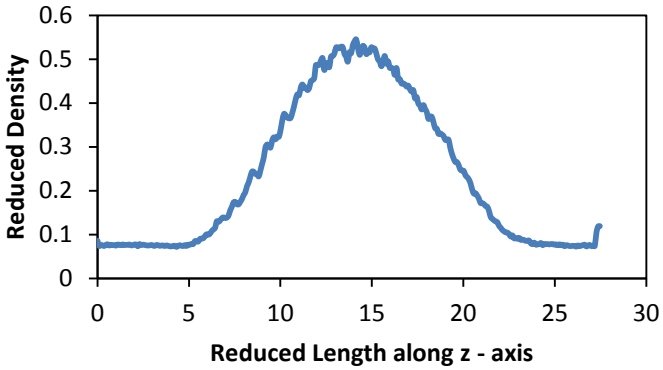

Figure 1: Density as a function of z-axis

Results:

As shown in Figure 1, there is a clear separation between the two phases. However, the density of the gas phase is much larger than that expected by comparison with the Mecke et al.[1] This is likely because either the size of the system was not large enough for good statistics, or the system was not completely equilibrated. It was noticed from the dynamics simulation movie, that the liquid phase was not completely stationary. If this is the case, then the density profile of the liquid will broaden like in Figure 1.

Additionally, there is a small deviation in the Figure 1 curve near $z = 27$, which would be fixed if the system was larger or the simulation was run for longer.

Conclusion:

The preliminary results are promising, as we have a clear separation of the phases, however in the future it will be necessary to ensure that the system is equilibrated. Also, we may need to add significantly more particles to ensure good statistics.

The next step is to add a second component and make the system a binary mixture. In a binary mixture you will be able to determine the surface tension along with the relative Gibbs surface excess of each species. The ability to predict the surface excess if very biologically relevant, since certain ions favor the liquid-vapor interface.

Supplementary Information (Movie):

Caption: Liquid-vapor interface of a Lennard-Jones system

References:

[1]Mecke, M., Winkelmann, J., Fischer, J. J. Chem. Phys. **110**. 1188-1194 (1999).