

MOLECULAR DYNAMICS SIMULATION OF EVAPORATION OF A TWO-COMPONENT LIQUID

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Abstract. We present an algorithm for molecular dynamics simulation of evaporation of a binary liquid for arbitrary subsonic Mach numbers. As expected, we observe an enrichment of the lighter component in the vapor phase as compared to the composition in the liquid.

Keywords: molecular dynamics, evaporation, two-component system

INTRODUCTION

In this paper we present an algorithm for doing molecular dynamics for evaporation of a binary liquid for arbitrary subsonic Mach numbers. The work is an extension of [1]. Since sampling in molecular dynamics is simpler if the system is steady, the chosen algorithm keeps the relative composition in the liquid constant in time. This is an artificial situation; in a reality, even if the saturation densities and the evaporation coefficients are equal for both species, the lighter component will evaporate faster, i.e. it has the largest evaporation flux, and hence leads to a depletion of the lighter component in the liquid phase.

MOLECULAR DYNAMICS

Molecular dynamics [2] techniques offer the possibility to study the liquid-gas interphase in detail. The translational motion of all the molecules in the simulation box is calculated according to Newtons second law

$$\mathbf{F}_i = m\mathbf{a}_i. \quad (1)$$

\mathbf{F}_i is the sum of all forces acting on molecule i , and it is often approximated as the sum of pair interactions between the molecules. The resulting system of nonlinear differential equations is solved numerically.

Our molecular dynamics simulation of one-dimensional steady evaporation in a half space, is conducted in an elongated box, see Fig. 1. The dimensions of the box are given by L_x , which is the longest side, and L_y and L_z that are equal. An elongated box with the liquid slab in the middle is used so the gas region can be relatively long with the number of liquid molecules limited. Periodic boundary conditions are used in the direction normal to the flow. In the x -direction, particles leaving the box are either reinserted on the other side or in the middle of the liquid, as will be explained in the next section. In the middle of the liquid there is a thermostat that keeps the temperature fixed. The thermostat has been implemented by scaling the velocity of the molecules in the thermostatted region, giving the desired kinetic energy and hence temperature. Fluctuations of the center of mass of the liquid can be larger than the width of the interface. Such behavior would smear out density profiles, etc. Therefore the liquid slab is kept in the middle by shifting the x -coordinates, this does not change the relative distance between the molecules. The shifting is determined by the requirement that there shall be an equal number of molecules in both halves of the box. The velocities of the molecules may also be rescaled at regular intervals so the momentum of the liquid slab is zero.

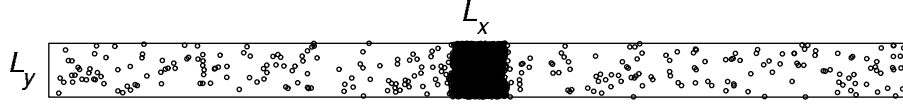


FIGURE 1. Simulation box.

Lennard-Jones-spline potential

In the simulations a Lennard-Jones-spline(LJ-spline) potential[5] has been used. The potential between two particles of species i and j is given by

$$U_{ij} = \begin{cases} 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r} \right)^{12} - \left(\frac{\sigma_{ij}}{r} \right)^6 \right] & r \leq r_s \\ k_1(r - r_c)^3 + k_2(r - r_c)^2 & r_s < r \leq r_c \\ 0 & r > r_c \end{cases} \quad (2)$$

where $r_s = \left(\frac{26}{7}\right)^{1/6} \sigma_{ij} \approx 1.24\sigma_{ij}$, $r_c = \frac{67}{48}r_s \approx 1.73\sigma_{ij}$, $k_1 = -\frac{387072}{61009} \frac{\epsilon_{ij}}{r_s^3}$ and $k_2 = -\frac{24192}{3211} \frac{\epsilon_{ij}}{r_s^2}$. Here σ_{ij} is the inter-molecular separation between a particle of species i and another particle of species j , where the pair-potential is zero, and ϵ_{ij} is the potential depth. The LJ-spline potential deviates from the Lennard-Jones potential only in the tail. A cubic spline is fitted from the point r_s of inflection so the potential goes smoothly to zero at r_c . Calculation of the forces with the spline potential is much faster than the conventional Lennard-Jones potential cut at $2.5 \sigma_{ij}$, since the neighbor list is much shorter with the LJ-spline potential. The LJ-spline fluid is a model fluid for spherical molecules, and it does not correspond exactly to any real substance.

The potential parameters for component 1, σ_{11} and ϵ_{11} , in addition to the molecular mass m_1 and Boltzmann's constant, are used to make nondimensional quantities, that are denoted by an asterisk. For example, $x^* = x/\sigma_{11}$.

EVAPORATION ALGORITHM

We now look at the right half of the simulation box in Fig. 1, the treatment of the other half differs only in the sign of the x -component of the velocity. The gas phase has length L where L is large enough so the fluid reaches the equilibrium flow conditions far out in the gas phase. In evaporation, only one parameter can be specified[3], here we chose the drift velocity at 'infinity'. The way the drift velocity is specified is to force the velocity distribution function at L for each component to be symmetric about u_∞ , as was done by Frezzotti[4] in a DSMC simulation of binary evaporation. No assumption on the shape of the distribution function is made, if the simulation domain is long enough the distribution should become a drifting Maxwellian. When a molecule with velocity c_x leaves the box at $x = L$, it is reinjected at the boundary with velocity $\mathbf{c}' = 2u_\infty \hat{\mathbf{x}} - \mathbf{c}$, if $c'_x < 0$, and with a probability $|c'_x|/c_x$. The probability condition follows from the ratio of the differential fluxes of the given species, for molecules entering, $|c'_x|n_\infty F_\infty(\mathbf{c}')$, and leaving the box, $c_x n_\infty F_\infty(\mathbf{c})$,

$$\frac{|c'_x|n_\infty F_\infty(\mathbf{c}')}{c_x n_\infty F_\infty(\mathbf{c})} = \frac{|c'_x|}{c_x} \quad (3)$$

since $F_\infty(\mathbf{c}') = F_\infty(\mathbf{c})$. Hence only a fraction $|c'_x|/c_x$ of the molecules with mirrored velocity $c'_x < 0$ should be reinjected. The temperature and hence Mach number is a result of the computation.

The molecules that are not allowed to reenter the gas domain are inserted in the liquid to maintain a steady evaporation flux. Just inserting the molecule at a random position in the middle of the liquid should not be attempted since this may cause large overlaps of the repulsive cores giving unphysically large repulsive forces and velocities. Instead we locate a small hole nearby the randomly chosen position and try to expand it in a controlled way. The algorithm works as follows : Pick the molecule nearest the random position chosen, here denoted molecule 1. Its closest neighbor is denoted molecule 2. A molecule 3 is chosen among the other successively nearest neighbors of molecule 1 so that the angle γ between the vectors $\mathbf{r}_2 - \mathbf{r}_1$ and $\mathbf{r}_3 - \mathbf{r}_1$ is between 25 and 95 degrees. The molecule removed from the gas is inserted in the middle of the triangle given by the center of the nodes, $(\mathbf{r}_1 + \mathbf{r}_2 + \mathbf{r}_3)/3$. This procedure is shown in Fig. 2. The algorithm ensures that there are no molecules closer to the inserted molecule than those in the triangle. Assuming a nearest neighbor distance of σ_{11} , the distances between the inserted molecule and the molecules at the nodes of the triangle are approximately $0.6 \sigma_{11}$. The forces are strongly repulsive and the inserted molecule creates a larger hole by itself. To avoid unphysically large velocities, the speeds of the inserted molecule and the 3 molecules in the triangle are rescaled for some time-steps after the insertion. The direction is maintained, but the

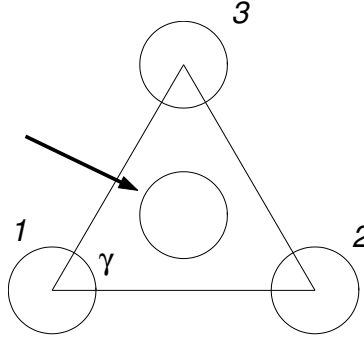


FIGURE 2. Insertion of a molecule in the liquid. The molecular diameter is not drawn to scale, the molecules actually have large overlaps.

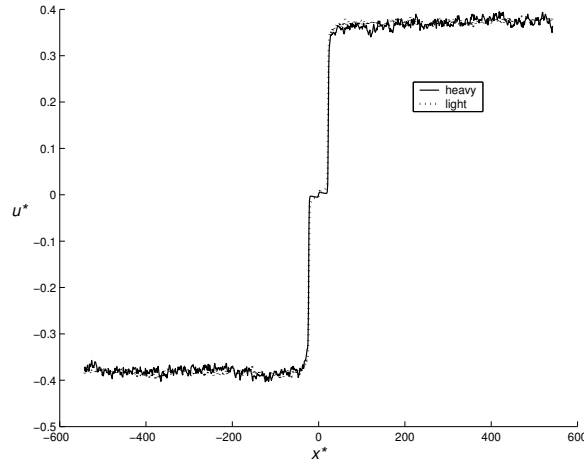


FIGURE 3. Plot of the velocities of the components.

speed is cut at 3 equilibrium standard deviations. The velocities are rescaled for so many time-steps it takes a molecule with the rescaled velocity to move $0.4\sigma_{11}$. After this procedure, the distances between the inserted molecule and the nearest neighbors are approximately σ_{11} . The excess kinetic energy is removed by the thermostat.

TEST SIMULATION

We use the Lennard-Jones-spline potential, with parameters $\sigma_{11} = 3.67\text{\AA}$, $\sigma_{22} = 3.405\text{\AA}$, $\epsilon_{11}/k_B = 167K$, $\epsilon_{22}/k_B = 119.8K$, $\sigma_{12} = \frac{1}{2}(\sigma_{11} + \sigma_{22})$ and $\epsilon_{12} = \sqrt{\epsilon_{11}\epsilon_{22}}$. The masses of the components are $m_1 = 83.8u$ and $m_2 = 39.95u$. If used with the full Lennard-Jones potential, these parameters correspond to the krypton-argon mixture. The simulation is conducted with 8000 atoms, 4000 of each component. The dimensions of the simulation box are $Lx = 1085\sigma_{11}$, $Ly = 14\sigma_{11}$, giving an aspect ratio of 80. The liquid slab has dimensions $40\sigma_{11} * 14\sigma_{11} * 14\sigma_{11}$ and contains approximately 5900 particles. The temperature of the thermostat in the liquid is $T_{liq}^* = 0.65$, and the set velocity at infinity is $u_{\infty}^* = 0.4$.

As in the one-component simulation [1] (a different, unrelated computer code), the specified velocity at infinity was not attained, but there is an undershoot, as can be seen in Fig. 3. This may be due to the fact that the molecular interactions are not represented correctly at the end of the box, and the distribution function may not be completely Maxwellian. An infinite box can not be simulated, so either ‘periodic’ forces or a vacuum boundary are used, but it turns out that both give the undershoot. We also tried longer equilibration and longer sampling after steady state was reached, but the results remained the same.

To rule out that it is the tricks to keep the liquid in the middle of the simulation box that give the anomaly, the

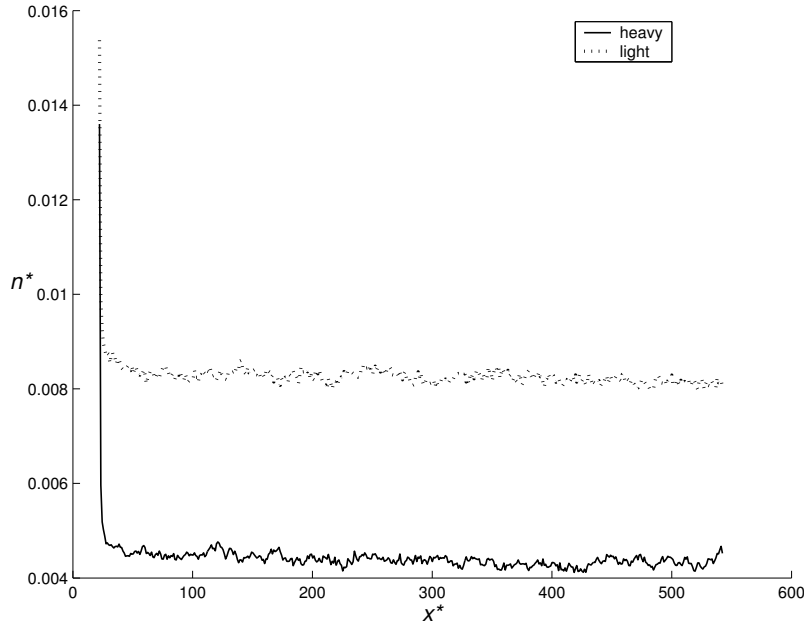


FIGURE 4. In the liquid the number-densities of the components are approximately equal, but as shown in the figure, in the vapor phase the lighter component is enriched.

liquid slab was replaced by the boundary condition used in DSMC solutions of binary evaporation [4]. However, the undershoot was still there. As a final test that the implementation of the boundary condition at the end of the box is correct, a copy of the boundary condition code was pasted into a DSMC code for evaporation of a two-component liquid, and then the set velocity was attained.

We did not manage to solve the undershoot problem. From the test run described above, the only logical conclusion is that the problem is related to how to represent the interaction with the fictional particles outside of the ends of the box. However, it seems weird that this should give such a profound effect given the low density in the vapor, and hence relatively few interactions.

However, regardless of the undershoot, we obtain velocity- and temperature-profiles that are stationary and flat far from the interface, as they should be. Hence, the solutions should be valid for the new drift velocity that deviates slightly from the set value. The resulting Mach number at infinity for the above simulation is then $M_\infty = 0.29$.

Fig. 4 shows a plot of the number density for the two components in the interface and in the vapor phase. Enrichment of the lighter component in the vapor relative to the composition in the liquid is observed, as was also the case for the DSMC simulation by Frezzotti[4].

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