Shear-induced mixing/demixing of a two component lubricant

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Abstract

We use classical molecular dynamics to investigate the role of shear on the phase separation of a liquid binary mixture. Our simulations show that, while shearing has no affect on Kr separation when it occurs spontaneously, shearing is instead quite effective in promoting a significant amount of clustering, and thus of phase separation over a time scale of a few ns.

Advisor: Dr. Nicola Manini
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1 Introduction

The phase separation between two fluids may occur spontaneously for thermodynamic reasons, as it happens in everyday life with the oil-water mixture. In certain regions of the phase diagram where the completely mixed state is thermodynamically stable, it is possible that the shear of the liquid can foster phase separation of dynamic nature, that might even lead to a reduction of friction.

We investigate this possibility by classical molecular dynamics simulations. We study the behavior of a lubricant placed between two rigid and parallel plates that can move in any direction. By convention we take one of them in a fixed position. For simplicity we simulate a noble-gas mixture, Argon plus Krypton, assumed to interact through the Lennard-Jones potential. The parameters $\epsilon$ and $\sigma$ of the like-pair interaction are taken from literature, and the parameters of the unlike-pair interaction are calculated by applying the Lorentz-Berthelot combining rules with an important correction.

The conclusion of our simulation is indeed that shear may promote, in certain regions of the phase diagram, a phase separation.
2 The Model

The model is composed by two parallel and rigid surfaces that we indicate with “top” and “bottom”, plus a number of lubricant atoms confined between them (Fig. 1). By convention, we take the bottom at a fixed position. The top can move rigidly in any direction and we can apply to it an external velocity and/or external forces. The lubricant is composed by two different species of atoms: Argon and Krypton. The atoms of the whole model interact with the Lennard-Jones-type two-body potential:

\[
\Phi_{ij}(r) = \epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r} \right)^{12} - 2 \left( \frac{\sigma_{ij}}{r} \right)^{6} \right],
\]

where \( i, j \) indicates the species of the two atoms. For the like-pair interaction we use the parameters given in [1] and collected in table 1. The unlike-pair parameters \( \epsilon_{12} \) and \( \sigma_{12} \) are calculated by applying modified Lorentz-Berthelot combining rules

\[
\epsilon_{12} = \delta_{12} \sqrt{\epsilon_{11} \epsilon_{22}},
\]

\[
\sigma_{12} = \frac{\sigma_{11} + \sigma_{22}}{2}.
\]

Here \( \epsilon_{ii} \) and \( \sigma_{ii} \) are the like-pair parameters and \( \delta_{12} \) is the binary interaction parameter, which give the possibility of artificially varying the unlike-pair interaction. In this work we always take \( \delta_{12} = 0.7 \) as in Ref. [2]. For simplicity in this work we assume that the Ar e Kr have the same mass, namely the Ar mass, 39.948 a.m.u..

The LJ interaction has an infinite range, but when \( r \) is large enough, the potential energy and the corresponding force becomes very small. In order to reduce the number of interaction that must be calculated, we introduce a cut-off radius \( R_c \) and we ignore the interaction with \( r \) larger than \( R_c \). This truncation of the potential creates an energy jump when the distance between particles crosses the cut-off value. In order to grant the energy conservation we shift the potential by the constant quantity \( \Phi_{ij}(R_c) \). Hence we redefine the potential as:

\[
\Phi^*_ij(r) = \begin{cases} 
\Phi_{ij}(r) - \Phi_{ij}(R_c) & \text{if } r < R_c \\
0 & \text{if } r > R_c
\end{cases}
\]

In this work we set \( R_c = 2.5 \cdot \sigma_{22} \), we select \( \sigma_{22} \) because it is larger than \( \sigma_{11} \). With this choice of \( R_c \) the energy that we neglect is \( Max[\Phi_{ij}(R_c)] \approx -8 \cdot 10^{-3} \epsilon_{22} \) per particle, which is a small amount of energy, with little influence on the demixing. This redefinition of the potential does not change the force for \( r < R_c \) because \( \nabla \Phi_{ij}(r) = \nabla \Phi^*_ij(r) \).
Figure 1: A sketch of the model

<table>
<thead>
<tr>
<th></th>
<th>$\epsilon/K_b$ (K)</th>
<th>$\sigma$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>117.5</td>
<td>0.3390</td>
</tr>
<tr>
<td>Kr</td>
<td>161</td>
<td>0.3607</td>
</tr>
<tr>
<td>Ar-Kr</td>
<td>96.3</td>
<td>0.3498</td>
</tr>
</tbody>
</table>

Table 1: Values of the LJ parameters for the Ar-Kr mixtures, the like-pair parameters are taken from Ref. [1], the unlike-pair parameters are calculated with [2].
2.1 The forces

The atoms of the lubricant can move in every direction, they interact with the other lubricant particles, with the top and with the bottom. The force on the \(i\)-th particle is:

\[
\vec{F}_i = -\sum_{j \neq i}^N \frac{\partial \Phi^*_{ij}(|\vec{r}_i - \vec{r}_j|)}{\partial \vec{r}_i} - \sum_{j}^N \frac{\partial \Phi^*_{it}(|\vec{r}_i - \vec{r}_j|)}{\partial \vec{r}_i} - \sum_{j}^N \frac{\partial \Phi^*_{ib}(|\vec{r}_i - \vec{r}_j|)}{\partial \vec{r}_i} \quad (4)
\]

where \(N, N_t, N_b\) are the numbers of lubricant, top and bottom particles. \(\Phi^*_{it}\) and \(\Phi^*_{ib}\) are the LJ truncated potential between the \(i\)-th particle of the lubricant and a particle of the top/bottom with \(\sigma = 1.02 \cdot \epsilon_{11}\) and \(\epsilon = \epsilon_{11}\). The bottom atoms are frozen in a perfect crystalline order.

The top is a rigid lattice that can move in any direction under the effect of:

- an external constant force \((F_{ext})\) in the \(z\)-direction in order to simulate pressure
- an external constant velocity \((v_{ext})\) in the \(x\)-direction
- the reaction forces due to interaction with lubricant

Thus the force on the top’s center of mass is:

\[
F_x = -\frac{1}{N_t} \sum_{i=1}^{N_t} \sum_{j=1}^{N_p} \frac{\partial \Phi^*_{ij}(r_{ij})}{\partial r_{ix}} + F_{ext}
\]

\[
F_y = -\frac{1}{N_t} \sum_{i=1}^{N_t} \sum_{j=1}^{N_p} \frac{\partial \Phi^*_{ij}(r_{ij})}{\partial r_{iy}}
\]

\[
F_z = -\frac{1}{N_t} \sum_{i=1}^{N_t} \sum_{j=1}^{N_p} \frac{\partial \Phi^*_{ij}(r_{ij})}{\partial r_{iz}}
\]

The position \(\vec{r}_t\) of the top center of mass move according to the forces of \((5)\), except for the \(x\) motion, which advances at exactly fixed speed \(v_{ext}\). When the motion of the top’s center of mass is resolved, one can build the position of all atoms of the top thanks to its rigidity.
2.2 The Langevin thermostat

To simulate the system at a fixed temperature we make use of the *Langevin thermostat* [3]. In the Langevin thermostat, at each time step all particles are perturbed by a random force and have their velocities damped by a viscous friction. Thus the $i$-th particle’s equation of motion are modified in this way:

$$m \ddot{r}_i = -\nabla_i U - m \gamma (\dot{r}_i - v_{CM}) + R_i(t),$$

(6)

where $U$ is the total potential, $\gamma$ is the viscous parameter (in reciprocal units of time), also known as the damping coefficient, and $v_{CM}$ is the speed of the lubricant center of mass. The random force $R_i$ is a Gaussian process with statistical properties given by:

$$\langle R(t) \rangle = 0 \quad \langle R(t) R(t')^T \rangle = 2\gamma K_b T m \delta(t - t')$$

where $K_b$ is the Boltzmann constant, $\delta$ is the Dirac symbol and $T$ is the target temperature. The damping coefficient and random force combine to give the correct canonical ensemble. In this work we always take $\gamma = 0$.

When all forces are calculated we integrate the equations of the motion using a 4th order Runge-Kutta method with an integration step of 0.0025 units of time. We have verified, in the $T = 0 \gamma = 0$ case (no thermostat), that energy is conserved very accurately.
3 Technical implementation

3.1 Natural units

We measure all quantities in a natural system of units, where length is measured in units of $\sigma_{11}$, mass in units of mass $m$ off all particles, and energy in units of $\epsilon_{11}$. This system is summarized in table 2. In this work, we express all physical quantities it in this natural system of units, except when specified explicitly.

<table>
<thead>
<tr>
<th>Physical quantity</th>
<th>Natural units</th>
<th>Real units</th>
</tr>
</thead>
<tbody>
<tr>
<td>length</td>
<td>$\sigma_{11}$</td>
<td>0.339 nm</td>
</tr>
<tr>
<td>mass</td>
<td>$m$</td>
<td>6.690 $\cdot 10^{-26}$ Kg</td>
</tr>
<tr>
<td>energy</td>
<td>$\epsilon_{11}$</td>
<td>10.125 meV</td>
</tr>
<tr>
<td>force</td>
<td>$\epsilon_{11} \cdot \sigma_{11}^{-1}$</td>
<td>4.785 pN</td>
</tr>
<tr>
<td>velocity</td>
<td>$\sqrt{\epsilon_{11}/m}$</td>
<td>155.7 m/s</td>
</tr>
<tr>
<td>time</td>
<td>$\sigma_{11}/\sqrt{\epsilon_{11}/m}$</td>
<td>2.187 ps</td>
</tr>
<tr>
<td>pressure</td>
<td>$\epsilon_{11} \cdot \sigma_{11}^{-3}$</td>
<td>4.16 $\cdot 10^{7}$ Pa</td>
</tr>
</tbody>
</table>

Table 2: Natural units of the system.

<table>
<thead>
<tr>
<th>$\epsilon/K_b$</th>
<th>$\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>1.00</td>
</tr>
<tr>
<td>Kr</td>
<td>1.37</td>
</tr>
<tr>
<td>Ar-Kr</td>
<td>0.82</td>
</tr>
</tbody>
</table>

Table 3: Values of the Lennard-Jones parameters (table 1) scaled in natural units.
3.2 Periodic boundary condition

To mitigate surface effects we impose periodic boundary conditions [4] in the x-y plane, we simulate only a relatively small box, the "supercell", and that is replicated throughout space to form an infinite lattice. In the course of the simulation, as a particle moves in the original box, its periodic image in each of the other boxes moves in the same way. Thus, as a particle leaves the central box, one of its images will enter through the opposite face. The supercell is generated by the following Bravais primitive vectors:

\[ \vec{a} = 1 \hat{x} + 5\sqrt{3} \hat{y} \]
\[ \vec{b} = -8 \hat{x} - 2\sqrt{3} \hat{y} \]

which form a 60° angle. In a supercell of this size and shape there fits an horizontal layer composed of 67 particles provided that they are arranged in a lattice rotated by \( \alpha_l = 24.49439053^\circ \) with respect to the x axis and with a lattice spacing of \( s_l = \sigma_{22} \). We have chosen the supercell size such it fits integer planes of Kr [5], which theme might find it advantageous form horizontal layers rather then localized clusters. The top and the bottom are also triangular layers of lattice spacing \( \sigma_{11} \) oriented along the x direction. The PBC have been chosen appropriately so that the substrate layers periodicity fits perfectly within the supercell.

3.3 Cell lists method

In a typical molecular dynamic code, the part of the program that take the most of the CPU time is the calculation of the forces. If we calculate every single bond length (even if it produces null force) we create an algorithm that scales \( \propto N^2 \). To avoid this difficulty we use the Cell lists method [6], which is an algorithm that scales with \( N \). In this method the supercell is divided into cells with a size slightly greater than the cut-off radius \( R_c \). Each particle in a given cell interacts only with the particles in the same or neighboring cells. The allocation of an atom to a cell is an operation that scales with \( N \), and the number of cell that needs to be considered is independent to the size of the system, both forces must be computed only within one cell and a fixed number of neighbouring cells, so that algorithm scales with \( N \). We have used this algorithm in the 2-dimensional version in the x-y plane.
4 Equilibrium simulations

We consider two concentrations: 60% Ar+40% Kr, and 90% Ar+10% Kr. For the 40%-Kr mixture we simulate 670 lubricant atoms, initially arranged in 10 layers. In the 10%-Kr mixture we simulate 1340 atoms. In this later case we double the number of layers in order to have enough Kr atoms to give them a chance to form a layer-cluster.

Initially the supercell takes the form represented in Fig. 2. To reach a well mixed situation we heat the lubricant at temperature $K_B T = 2$. After sufficiently long time we cool the lubricant down to temperature $K_B T = 1$, going through an intermediate step. We summarize the duration of the steps in table 4. The 10% Kr mixture need a longer annealing time because of the larger vertical size. The annealing process is carried out with no dragging of the top layer. After this annealing procedure, typical configurations are shown in Fig. 3. Starting with these well mixed configurations we proceed to cool the mixture down to the target temperature $K_b T = 0.889$, and we set the pressure to 0.1($F_{ext} = 6.58$ ). In this point of the phase diagram we expect that the 40%-mixture should have phase separation, but not the 10%-mixture, as was shown in Ref. [2]. Indeed our expectations are confirmed by simulations: Fig. 4 shows the supercell of the 40%-mixture after 700 time units (1.53 ns) and the supercell of the 10%-mixture after 1500 time units (3.28 ns). It is evident that clustering of Kr has occurred in 40% simulation, while in 10% there are no sign of clustering, despite the rather long time. While segregation cannot be excluded over longer time scales, our simulations at least suggest that this phenomenon occurs very slowly.

To describe quantitatively the tendency to segregation, we define and compute the average connectivity $S(t)$ that is the average number of Kr atoms bonded to each Kr atom at time $t$. Conventionally we define ”bonded” if the atom is placed within a sphere of radius $1.3 \cdot \sigma_{22}$ of the first one. For comparison, in the initial order state (Fig. 2) $S(0) \simeq 14$ for the 40% case and $S(0) \simeq 12$ for the 10% case.

In a fully disordered state one expects $S(t)$ to fluctuate around a value mean the concentration of Kr multiplied by the average number of atoms surrounding a given Kr atom, approximately 10.

To have more reliable date, and to make sure that the final data do not depend on a specific starting condition we repeated the annealing process and we obtain 5 different starting conditions. Each of them is obtained starting from the final configuration of the $K_b T = 2$ simulation and continuing the the simulation for different time units, after which we follow the process show in table 4. Figures 5(b) and 5(a) display the time evolution of $S(t)$ of the two mixtures. The
plots show very different behaviour of the 40% and 10% situations. In the 40% case, the average connectivity clearly increases from a value indicator of high disorder ($\sim 6$) up to $S \gtrsim 9$, indicator of substantial clustering, while in the 10% simulations the Kr atoms remain scattered and $S(t)$ fluctuates around 2.5.

\[
\begin{array}{c|cc|cc}
K_b T & 40\% Kr & 10\% Kr \\
\hline
2 & 1 & 200 & 300 \\
1.5 & 0.5 & 50 & 100 \\
1 & 0.2 & 50 & 100 \\
\end{array}
\]

Table 4: The duration of the annealing process (in natural units) to prepare a well mixed configuration (Fig. 3) starting from the initial fully ordered configuration at Fig. 2.

Figure 2: Initial configuration of the lubricant. Smaller white balls represent Ar atoms, bigger green balls are the Kr atoms.
Figure 3: Configuration of the lubricant at the end of the annealing process at the final temperature $K_b T = 1$. This type of configuration is taken as the starting point of the actual simulations.
Figure 4: Final snapshot of the lubricant at the end of rather long simulations carried out at $K_b T = 0.889$, with no dragging of the top layer. (shear $\dot{\gamma} = 0$)
Figure 5: The average Kr-Kr connectivity measured in the 2 Kr mixtures and in 5 runs starting in from 5 independent initial condition, all done without shearing. The black thick line is the average over the 5 values.
5 Sliding Simulations

To investigate if shearing the lubricant might have any affect on phase separation, we make the top advance at a fixed velocity $v_{\text{ext}}$, thus inducing a shear rate $\dot{\gamma} = v_{\text{ext}}/d$, where $d$ is the liquid film thickness, that we take $d = \langle z_{\text{top}} \rangle - \sigma_{11}$. We find that shear does not modify the behaviour of the 40%-mixture as shown by $S(t)$ plotted in Fig. 6. But it seems to have some ordering effect on the 10%-mixture. When simulations is done under shearing the final configurations of the 10%-mixture have some signs of clustering (Fig. 7) indeed the average connectivity $S(t)$ increases significantly (Fig. 8) going from 2.5 to 3.5, while the simulations without shear fluctuates around 2.5. Shearing is therefore effective in clustering of Kr, and therefore a certain level of phase segregation. This is the main result of the present thesis.
Figure 7: The five final configurations of the lubricant at $K_b T = 0.889$, after 1500 time units. Simulation under shear due to $v_{ext} = 0.5$.
Figure 8: Like Fig. 6 but for 10%-Kr mixture. The shear rates are $\dot{\gamma} = 2.46 \cdot 10^{-2}$ and $\dot{\gamma} = 4.92 \cdot 10^{-3}$. This figure presents the main result of the present thesis: while no phase separation is seen to occur under equilibrium conditions, a significant amount of Kr clustering is induced by shearing.
5.1 Friction

To investigate possible effects of phase segregation on friction, we plot the $x$ component of the forces acting on the top, which is equal and opposite to the force that the external agent needs to apply to the top layer in order to keep it advancing at constant speed $v_{ext}$. To reduce the noise, we average over five independent simulations. Red thin line of Fig. 9 shows the friction as function of time: despite averaging, data are still rather noisy. For better appreciation of the global trends we smooth, by convolution with a Gaussian of width 0.01, thus producing the black line of fig 9. This friction clearly fluctuates around 16.5 (79 pN) but no clear increasing or decreasing trend is visible. The outcome of the 10% Kr simulations is entirely analogous. We thus conclude that segregation has little or no effect on friction.

![Figure 9: Friction of the top with $v_{ext} = 0.5$ for the 40% Kr mixture, obtained with averaging over 5 independent simulations. The red thin line is the real data, the black is the result of a smoothing process.](image-url)
6 Discussion and conclusion

In summary we verified that the liquid mixture of Ar and Kr does indeed show phase separation at temperature $K_b T = 0.889$ ($T \simeq 104$ K) and pressure $P = 0.1$ ($\simeq 4.16$ MPa) with a 40% fraction number of Kr as predicted in the literature [2]. For the 10% Kr fraction, the [2] predicts that this mixture should not separate. Indeed equilibrium simulations show the average connectivity remains roughly constant (see Fig. [8]) and compatible to highly mixed state over 1500 time units ($\simeq 3.3$ ns).

The new finding of the present work is the ordering effect of an applied shear, which promotes phase separation even in the 10% Kr mixture where segregation is thermodynamically unfavorable.

Further investigation would be required to confirm these preliminary findings. In particular, longer simulations could unveil possible further clustering. Size effects should also be investigated. A set of simulations starting from the final configurations of Fig. [7] but with no shearing could rule out the possibility that phase separation might be favored by thermodynamics even in the 10% Kr mixture. Other values of concentration should also be investigated to delimit the region of the phase diagram where this effect takes place. Different masses of the two species should also be considered. It is quite possible that when these masses differ significantly, the formation of a Kr layer might indeed screen the propagation of high frequency waves across the lubricant, possibly inducing a detectable friction reduction.
References


