Evaporation of R32/R1234yf Mixture on the Wall: A Molecular Dynamics Study

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Abstract. The mixed refrigerants have a great potential in the energy industry, while the micro-mechanism of evaporation of mixed refrigerants is still unclear. Therefore, molecular dynamics simulations were employed to investigate the evaporation of the R32, R1234yf and their mixture on the Pt surface at 230 K, 250 K and 350 K, respectively. The results indicate that the presence of R1234yf will suppress the evaporation of R32. The adsorption interaction between R32 and substrate is lower than that of R1234yf. The film boiling is found at high temperature evaporation. Meanwhile, the heat flux of the system decreases due to the heat transfer deterioration.

1. Introduction

In the past decades, with the rapid development of computer science, computer simulation technology has been widely applied in experimental research. Molecular dynamics simulations (MD) has proven to be a powerful tool to reveal micro/nanoscale mechanisms [1-32]. In fact, MD has been successfully applied to the study of vapor-liquid equilibrium of refrigerant mixtures, the condensation process of HFO refrigerants and to reveal the surface evaporation mechanism of simple fluid systems. Wael et al. [33] used the MD method to study the properties of 2,3,3-tetrafluoropropene (HFO-1234yf), trans-1,3,3-tetrafluoropropene (HFO-1234ze(E)), propane (isobutane, HC-600a), HFO-1234yf/HC-600a and HFO-1234ze(E)/HC-600a binary mixtures. Cai et al. [34] investigated the evaporation process of R32/R152a mixtures on the plane surface.

Due to the wide variety of working fluid mixtures, the surface evaporation characteristics of the working medium mixture need further study [35-37]. The R32 and R1234yf in the fourth-generation refrigeration working medium have great application potential. Many scholars have tested their properties, but the related performance of the mixed working medium needs to be further studied. Therefore, the paper employs the MD to investigate the evaporation of pure refrigerants R32, R1234yf and R32/R1234yf mixture on the Pt surface. The work is also expected to shed useful insights in fluid-solid interaction at nanoscale [38-45].

2. Simulation Details

2.1. Molecular model

The molecular model of R32 and R1234yf are built by Materials Studio software [46] and shown in Fig. 1. Also, the thermophysical properties [47] of R32 and R1234yf are listed in Table 1.
Table 1. The thermophysical properties of R32 and R1234yf

| Refrigerants | Structure | Standard boiling point/°C | Critical temperature/°C | Critical pressure/MPa | Critical density/(kg/m³) | ODP | GWP |
|--------------|-----------|---------------------------|-------------------------|-----------------------|--------------------------|-----|-----|
| R32          | CH₂F₂     | -51.651                   | 78.105                  | 5.782                 | 424.0                    | 0   | 675 |
| R1234yf      | CF₂CF=C=C ᴨ₂ | -29.45                  | 94.70                  | 3.38                  | 475.55                   | 0   | <1  |

The modeling system consists of fluid refrigerants and solid platinum (Pt) substrate, which Pt is widely used in MD to study fluid-solid interactions [48, 49]. The substrate consists of 700 atoms with 27.7 Å, 27.7 Å, and 13.7 Å in X, Y, and Z dimensions, respectively. Besides, the substrate is divided into NVT ensemble and fixed parts from top to bottom [50]. The Nose-Hoover thermostat is employed to control the temperature [51]. The volume of the simulation box is 27.7 Å×27.7 Å×800 Å (X×Y×Z). Periodic boundary conditions are applied in the X and Y directions. The Pt atoms fixed at the bottom and the ideal wall along the Z axis at the top are the boundaries in the Z direction.

2.2. The force field and governing parameters

The molecular interaction potential plays as an important role in MD. Since the present work focus on the evaporation characteristics of R32/R1234yf, the Lennard-Jones (12-6) potential model is employed to simulate the interactions between atoms in the studied systems. More details about the potential are described elsewhere [34].

The MD simulations are performed by the large-scale atomic/molecular parallel simulator (LAMMPS [52]). Time step is set as 1 fs (10-15s). Initially, the systems are equilibrated at 120 K for 3,000,000 steps. In order to trigger evaporation, the Pt atoms in the NVT part are rapidly heated to 230 K (above the boiling point of R32, 221.5 K), 250 K (above the boiling point of R1234yf, 243.7 K) and 350 K. At the same time, the fluid molecules are controlled by the NVE ensemble. In all simulations, the fixed platinum atoms always remain frozen. The evaporation process lasts for 1,000,000 steps. And atom information is stored every 1000 steps to analyze the results.

3. Results and discussion

3.1. Relative evaporation molecules during evaporation

After the equilibration, the relative evaporation molecules during the evaporation process are calculated and plotted in Fig. 2 (evaporation at 230 K), Fig. 3 (evaporation at 250 K) and Fig. 4 (evaporation at 350 K), respectively. The definition of evaporated molecules is the fluid molecules which 10 Å away from the adsorption film of the platinum substrate. And the relative evaporating molecules is the number of evaporated molecules divided by total number of initial molecules [53].
As shown in Fig. 2, all fluid samples have no evaporation during the initial evaporation period (from 0 to 180 ps) at 230K. This is because the thermal energy generated from the NVT substrate needs to heat the fluid system firstly. After that, as the simulation time increases, the relative evaporation of R32 molecule increases faster than that of R1234yf molecule. Also, R32 molecule starts to evaporate earlier than R1234yf. In the mixture system, it can be found that the addition of R1234yf slows the evaporation of R32. In other words, the addition of R32 will promote the evaporation of R1234yf. Also, the evaporation rate of R32 in the mixture system is obviously lower than that of the pure R32 system when the simulation time is long enough. However, the evaporation rate of R1234yf is almost the same in the studied systems by the end of simulation. The reason is that 230 K is the temperature between the boiling points of R32 and R1234yf. Although the evaporation rate of R1234yf in the mixture system is increased, there is no boiling during the entire simulation process and the maximum evaporation rate will not be significantly increased (boiling). However, the evaporation rate of R32 at 230K is reduced by R1234yf in mixture system, which ultimately leads to the lower evaporation rate than that of pure R32 system.

Fig. 2 Relative evaporation molecules during evaporation at 230 K

Fig. 3 Relative evaporation molecules during evaporation at 250 K
As shown in Figure 3, the delayed evaporation phenomenon also exists in the evaporation of 250 K. In addition, the evaporated molecules of R32 and R1234yf in all systems at 250 K are much more than those at 230 K. However, due to the relatively low temperature, the influence of the two working fluid on each other is still not obvious. The evaporation curve of R1234yf in the mixed working medium is almost the same as that of pure R1234yf during the entire evaporation process. In other words, R1234yf is hardly affected by R32. Additionally, the relative evaporation molecule value of R32 in the mixture system is slightly lower than that of pure R32 system. It indicated that R1234yf has an inhibitory effect on the evaporation process of R32.

The Fig. 4 shows the relative evaporation of fluid molecule in the studied systems at 350 K. At this time, R1234yf still has an inhibitory effect on the evaporation process of R32 and this effect increases as the temperature increases. Besides, in other words, the R32 have a promotion effect on the evaporation process of R1234yf.

The conclusions can be drawn through the comparison of the three figures (Fig. 2, Fig. 3, and Fig. 4). The evaporation rate of R32 and R1234yf is slow when the temperature is low. In the mixed working medium, R32 can significantly increase the relative evaporation of R1234yf. And vice versa, R1234yf has the suppression effect on the evaporation process of R32. The relative evaporation amount and evaporation rate of the two working fluids increase greatly when the temperature is high. Besides, the relative evaporation amount of R32 is higher than that of R1234yf.

Under the conditions of 230 K and 250 K, the amount of evaporated molecules is small. Therefore, the evaporation snapshots of the three systems at 230K and 250K are not listed here. The evaporation snapshot of the system at 350K is shown in Figure 5. Obviously, the increased thermal energy generated by the substrate leads to enhanced evaporation at 350 K, which promotes the boiling of the Pt substrate surface. Moreover, the nucleate boiling of the refrigerant fluid can improve the heat transfer of the Pt substrate and increase the heat dissipation of the substrate. In that way, it can prevent the substrate from overheating. Besides, the film boiling of the liquid refrigerant causing a large amount of refrigerant molecules to evaporate and boil. In this study, it can be obtained that a large number of bubbles coalesce at a temperature corresponding to about 500 ps. In theory, a vapor film will be formed above the Pt substrate in behind. The presence of the vapor film will increase the heat transfer resistance after 500 ps that resulting in deterioration of the heat transfer of the evaporation system. And the evaporation rate will slow down.
3.2. Temperature distribution and particle distribution during evaporation

Temperature distribution and particle distribution on the Z axis of the simulated evaporation system at 230 K, 250 K and 350 K are calculated and plotted in Fig. 6, Fig. 7 and Fig. 8, respectively. The simulation results indicate that 0-15 Å is the Pt substrate. But the 0-15 Å part is not shown in the particle distribution diagram.

As it shown in the temperature profile, there is a temperature jump at the interface between Pt substrate and the fluid. As the distance between the fluid and the Pt surface increases, the temperature of the fluid working medium tends to decrease. This is because fluid molecules are the carrier of thermal energy. In other word, evaporated molecules take away the heat of the system. Comparing the three figures, it can be found that the working medium temperature of the pure R32 system is always lower than that of the pure R1234yf and mixed working fluid systems. It indicates that the R32 molecules largely evaporate and cool the wall.

In the three particle distribution diagrams, the number of molecules near the surface of Pt is large. The reason is that there is a strong adsorption interaction between the Pt substrate and the fluid. In this way, a layer of dense and regularly arranged refrigerant molecules is adsorbed on the surface of Pt substrate. As the increase of the distance from the Pt substrate, the adsorption force of the substrate on the working molecule molecules becomes smaller. Thus, the particle distribution curve drops sharply in this area. In addition, film boiling has little effect on the number of molecules in the adsorption layer. As the temperature increases and the number of molecules at the same position gradually decreases, it indicates that the higher the temperature and the faster the working substance evaporates. The mixed working fluid curves in the three figures show that R32 and R1234yf are always mixed evenly at three temperatures and the molecular ratio is maintained at 1:1.
3.3. The heat flux during evaporation

The heat flux of the three systems through the evaporation zone on the Z axis during evaporation at 350K are calculated and plotted in Fig. 9. It can be found that in the initial stage of the evaporation process (0-200 ps), the heat flux of these three systems almost fluctuates around a fixed value. It is due to the heat transfer of the Pt substrate. The refrigerant is heated up from the equilibrium state of 120K. At this time, few molecules evaporate from the liquid phase. The heat flux is mainly caused by the heat conduction of the liquid phase molecules. In this period, the value does not change much. After that, the heat flux of the three systems gradually increases as the simulation going. This is because more and more molecules leave the liquid phase and enter the vapor phase through the liquid-vapor interface. Please noted that in the pure R32 system, the heat flux increases abruptly during the period of 400-500 ps. This is due to the film boiling in the liquid film area, which causes a large amount of liquid to leave the Pt surface. After this, as the simulation proceeds, the heat flux of the pure R32 system begins to decrease after 600 ps. This is also because the film boiling phenomenon occurs in the system. Due to the insulating characteristics of the vapor film, the heat exchange between the Pt substrate and the working medium is become worse and the heat transfer performance of the system is deterioration.

The trend of the three curves coincides with the previous evaporation results. In the beginning, the working medium heats up and the heat flux fluctuates around a fixed value. Then the heat flux gradually increases with time which due to boiling in the liquid film area. Finally, the heat flux begins to decrease due to the appearance of film boiling.
4. Conclusion
In this paper, the molecular dynamics method is used to simulate the evaporation process of pure R32, pure R1234yf and R32/R1234yf mixture on Pt substrate at 230 K, 250 K and 350 K from the atomic scale with the analyzing the factors such as relative evaporation molecules, temperature distribution, adsorption of atoms and heat flux. The conclusions are conducted as following.

(1) The addition of R32 in the mixed working medium can increase the relative evaporation molecules of R1234yf, but the presence of R1234yf will inhibit the evaporation of R32. The relative evaporation amount of various working medium molecules will increase greatly when the temperature is higher.

(2) The nucleate boiling and film boiling is found at 350 K. At the same time, the presence of R32 molecule can accelerate the nucleate boiling of R1234yf.

(3) The adsorption capacity of R1234yf on the Pt surface is always better than that of R32.

(4) During the heating process of the working medium, the system heat flux fluctuates at a certain value. As the fluid molecules evaporate, the heat flow gradually increases. During the film boiling and heat transfer deteriorated, the heat flux of the system began to decrease.

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