

# Molecular Dynamics Simulation of Interfacial Phenomena in Two-Phase Flow: A Review

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## ABSTRACT

An attractive feature of the application of Molecular Dynamics (MD) simulation to the liquid-vapor interface in two-phase flow is that the method, well suited for the small length-scale region which may be size-affected, can be applied in multi-scale modeling together with continuum approach for the rest of the domain. Various studies have been reported in literature where the method has been utilized to analyze the interfacial regions in two-phase flow systems. In this article, the major investigations involving Molecular Dynamics analysis applied to interfacial phenomena in two phase flow and heat transfer systems are reviewed, with a focus on the thermodynamic, fluid dynamic and structural properties of the liquid-vapor interface. Discussions on the nature and premises of the reported work and a compilation of the salient features and major results are presented.

## NOMENCLATURE

$D$	=	diffusion coefficient, $m^2/sec$
$k_B$	=	Boltzmann constant, $J/K$
$N$	=	number of molecules
$r_c$	=	cut off distance between molecules, $nm$ or $\text{\AA}$
$T$	=	temperature, $K$
$t$	=	interface thickness, $\text{\AA}$
$t_d$	=	interface thickness based on density profile, $\text{\AA}$
$t_u$	=	interface thickness based on energy profile, $\text{\AA}$
$t_d^{el}$	=	interface thickness obtained from ellipsometry, $\text{\AA}$
$T_r$	=	reduced temperature
$x$	=	mole fraction
$z$	=	distance from the wall

## Greek symbols

$\alpha$	=	condensation coefficient
$\Delta t$	=	time step, $fs$
$\epsilon$	=	energy parameter of potential function, $J$
$\gamma$	=	surface tension, $N/m$
$\rho$	=	density, $kg/m^3$
$\sigma$	=	length parameter of potential function, $\text{\AA}$

## Subscripts and Superscripts

$c$	=	critical
$l$	=	liquid
$v$	=	vapor
$*$	=	reduced property

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## 1. INTRODUCTION

Phase change processes have various important technological applications, and hence a clear knowledge of interfacial phenomena related to phase change is essentially required in the design of such systems. Applications of phase change heat transfer are diverse, ranging from large heat exchange devices, process equipment and refrigeration systems, to thermal control of micro electronics and miniaturized electromechanical systems. As the phase change and related mass transfer are essentially interfacial phenomena, analysis of interfaces is required to understand the physical process and to optimize the design of phase change devices. At the macroscopic level, interfaces can be considered as the locations where the net conversion of one phase to the other occurs in the vaporization and the condensation processes. At the microscale and nanoscale level, the interface is a region between the bulk phases across which the mean molecular density exhibits a gradual transition between the bulk vapor and liquid. Experimental measurements on the truly nanometer sized interfaces are difficult to accomplish. In addition, the thickness of the interface would be such that the continuum assumption cannot be used, and so a discrete molecular level analysis would be ideal for an accurate investigation of interfacial properties.

Molecular Dynamics computations offer a powerful tool to simulate and analyze physical phenomena, and obtain thermophysical and strength-related properties in small scale and size-affected domains [39]. In many interesting problems, this method can be used together with conventional continuum modeling methods, to evolve multi-scale modeling strategies. One of such situations is the analysis of two phase flow domains, with or without phase change occurring during the flow, where the interfacial regions can be analyzed effectively with Molecular Dynamics simulations.

A large number of studies based on Molecular Dynamics have been reported, in connection with interfacial phenomena. A review of some of the major investigations, with a focus on the structural, thermodynamic and dynamic properties is presented in the sections to follow.

## 2. REVIEW OF THE LITERATURE

A summary of the research on Molecular Dynamics simulations for the analysis of interfacial phenomena undertaken by various investigators during the recent past are presented in Table 1. These investigations pertain to coexisting systems with different liquid-vapor combinations. In each of the work reviewed, the potential functions used in the analysis and the parameters studied are listed. The salient results and observations are also shown.

Analyses leading to the estimation and prediction of various interfacial properties namely the density, interface thickness, pressure, temperature, surface tension, diffusion coefficient, condensation/evaporation coefficient and the structural orientation are reviewed. In most of the cases, the typical simulation system chosen by investigators is the liquid slab with the vapor region on both sides. The general methodology is as follows: When the liquid layer is thick enough, a bulk property for the liquid can be obtained at the central region and also, the two liquid-vapor interfaces can be realized. The interfacial properties can then be predicted with reasonably good accuracy with the simulation method, applying time-averaging [35].

Discussions on the major studies are presented below, based on the focus of the analysis. Comparisons of the results from different investigations have been presented by classifying them as appropriate, and discussed below.

### 2.1. Density and interface thickness

The density profiles across the interface, and the interfacial thickness, have been determined for different fluids using MD simulations. Results obtained with an assumption of the Lennard-Jones potential (L-J fluids), water, alcohols and refrigerants are considered for a comparison. In the case of MD simulations, the potential function is the primary parameter that determines the accuracy of the simulation. Predicted density profiles are found to be qualitatively similar for almost all fluids, both in their shape and the temperature dependence.

Table 1. Summary of investigations on interfacial phenomena in two phase flow.

Nature of work	Features of MD Simulation	Observations and conclusions	Reference
<b>Water and L-J fluids</b>			
Simulation of the thermodynamic properties and orientational structure at the liquid-vapor interface.	Water :-Potential: CC, N = 1000, $r_c = 12\text{\AA}$ , $\Delta t = 0.5\text{fs}$ , L-J fluid:- Potential: L-J, $r_c = 15\text{\AA}$ , $\Delta t = 5\text{fs}$ .	<ul style="list-style-type: none"> <li>Density, surface tension and structural orientation were studied for water and L-J fluids.</li> <li>Compared the values of interface thicknesses calculated from the density profile, from energy profile, and also from the experiment for both water and L-J fluids.</li> <li>Simulated surface tension values for water are very low compared to experimental results.</li> <li>Two types of orientation ordering were found.</li> </ul>	Matsumoto and Kataoka (1988) [1]
Influence of polarization of water molecules on the interfacial properties.	Potential : TIP4P N = 432, $r_c = 0.92\text{nm}$ T = 290K, $\Delta t = 2.5\text{fs}$ Integration: Verlet.	<ul style="list-style-type: none"> <li>Performed MD simulation using standard TIP4P model and its polarizable version.</li> <li>Structure of polarizable water is found to be same as that of non polarizable water, as expected.</li> </ul>	Motakabbir & Berkowitz (1991) [6]
Studies on the structure and properties of liquid-vapor interface of water.	Potential: Lemberg-Stillinger-Rahman (LSR). N = 512 & 1000 Integration: Verlet T = 300K.	<ul style="list-style-type: none"> <li>Compared the results of LSR model with model using ST-2 potential.</li> <li>Interface width is in good agreement with the experimental value.</li> <li>As density decreases in the transition region the hydrogen bond breaks and tends to dimer formation.</li> <li>Diffusion coefficient at the interface is found to be higher than in the bulk.</li> </ul>	Townsend & Rice (1991) [2]
Surface phenomena of molecular clusters.	Water :-Potential: ST-2, N = 512, $\Delta t = 1\text{fs}$ Integration: -predictor corrector, Argon: - Potential: L-J, N = 864, $\Delta t = 10\text{fs}$ .	<ul style="list-style-type: none"> <li>Liquid droplets of water and argon surrounded by their vapor are simulated.</li> <li>Based on the number of neighboring molecules, each molecule is categorized as liquid, interface or vapor molecule.</li> <li>Life time of 'surface' regime of a molecule is about 50ps for both condensation and evaporation processes.</li> <li>Density distribution obtained is found to be different from the corresponding saturated value.</li> <li>Surface tension estimated for the argon cluster reproduces the order of magnitude and temperature dependence of bulk value.</li> </ul>	Maruyama et al. (1994) [3]

Table 1. (Continued)

Table 1. Summary of investigations on interfacial phenomena in two phase flow. (Continued)

Nature of work	Features of MD Simulation	Observations and conclusions	Reference
Simulation of the orthobaric density and surface tension of water.	Potential: SPC/E Long range: Ewald sum T = 315K–573K.	<ul style="list-style-type: none"> <li>• Orthobaric densities and surface tension of water were calculated.</li> <li>• Surface tension decreases with increase in temperature and is in excellent agreement with experiment.</li> <li>• Long range interaction is observed to be very important for the surface tension.</li> <li>• SPC/E model could accurately reproduce the experimental values of interfacial properties than either SPC or TIP4P.</li> </ul>	Alejandro et al. (1995) [4]
MD simulation of the liquid-vapor interface of water.	Potential: SPC/E $\Delta t = 1fs$ , $r_c = 9\text{\AA}$ Ensemble: NPT + NVT.	<ul style="list-style-type: none"> <li>• The structural and dynamic properties of liquid-vapor interface were calculated.</li> <li>• Compared the simulation results with existing experimental and simulation data.</li> <li>• SPC/E potential adequately describes the interface than other models.</li> <li>• Orientation of <math>H_2O</math> molecule varies as a function of distance from the interface.</li> <li>• Self diffusion coefficient of water is found to be larger at the surface than in the bulk.</li> </ul>	Taylor et al. (1996) [5]
Studies on water clusters, liquid and liquid-vapor interface with many body potentials.	Potential: Rigid, four site polarizable interaction potential, N = 550, $\Delta t = 2fs$ , $r_c = 9\text{\AA}$ T = 298K Ensemble: NPT.	<ul style="list-style-type: none"> <li>• A rigid four- site, polarizable water interaction potential is developed using MD method.</li> <li>• Using this potential the thermodynamic and structural properties of water clusters, liquid and liquid-vapor interface were calculated.</li> <li>• Density profile for the liquid- vapor interface agrees with other models in the literature. The interface thickness was estimated as 3.2Å at 298K.</li> <li>• Total and induced dipole moments of water molecules decrease as they approach the interface and reach values close to the gas phase.</li> <li>• The surface tension was calculated using the developed potential, which is in good agreement with corresponding experimental value.</li> </ul>	Dang & Chang (1997) [7]
Vapor-liquid equilibrium simulations.	Potential: SCPDP Integration: Gear predictor- corrector N = 1000 $r_c = 12.88\text{\AA}$ T = 300K–520K.	<ul style="list-style-type: none"> <li>• Orthorhombic densities, vapor pressure, surface tension and interface thickness were calculated for the SCPDP model of water using NVT-MD and GEMC methods.</li> <li>• Results from both methods agree with each other especially at low temperatures in the range 300–450 K.</li> <li>• Low value of critical temperature of SCPDP model makes the properties in disagreement with experimental data.</li> <li>• Predicted value of interface thickness showed better agreement with experimental result than SPC/E model.</li> </ul>	Rivera et al. (2002) [8]

Diffusion coefficient at liquid-vapor interface.	Potential: TIP4P/FQ Long range: PPPM Constrained: RATTLE $\Delta t = 1$ fs.	<ul style="list-style-type: none"> <li>Developed a general method to calculate self diffusion coefficient in the bulk and at the interface.</li> <li>Diffusion coefficient is found to be high at the interface than in the bulk.</li> </ul>	Liu et al. (2004) [28]
Thin water layer evaporation and evaporation coefficient	Potential: TIP4P, $r_c = 9\text{\AA}$ , $N = 1000$ Integration: -Gear predictor-corrector.	<ul style="list-style-type: none"> <li>Mechanism of evaporation of thin water layer in to vacuum was investigated.</li> <li>The simulated liquid and vapor densities agree fairly well with tabulated data and other simulation models</li> <li>Interface thickness increases approximately linearly with increase in temperature.</li> <li>Microscopic physical phenomena near liquid-vapor interface were studied.</li> <li>Due to the influence of hydrogen bonding at the interface a reduction in the evaporation coefficient was observed.</li> </ul>	Yang & Pan (2005) [9]
Methodology to analyze thin film featuring polyatomic fluids like nitrogen and water on solid metallic surfaces.	Water: Potential: SPC/E, $\Delta t = 0.5$ fs Long range: Ewald Nitrogen: -Potential: 2CLJD, $\Delta t = 0.5$ fs $T_f = 0.55$ .	<ul style="list-style-type: none"> <li>Mass density was predicted and plotted for both nitrogen and water.</li> <li>Both plots show the appearance of the wall affected, bulk liquid, interfacial, and bulk vapor regions.</li> <li>The calculated bulk liquid density and surface tension agree with ASHRAE recommended values.</li> </ul>	Wemhoff & Carey (2005) [10]
Influence of particle-particle particle-mesh method.	Potential: SPC/E Long range: PPPM, $N = 800$ , $r_c = 0.98$ nm, $\Delta t = 1$ fs, Integration: Verlet, Constraint: SHAKE, $T = 300\text{--}600$ K Ensemble: NVT	<ul style="list-style-type: none"> <li>Density and surface tension of water were determined for a range of temperature from 300–600 K.</li> <li>At low temperatures, the density and surface tension values agree well with experimental results.</li> <li>Deviation of the simulated values from the experimental values at high temperatures shows that SPC/E model is not accurate for high temperature simulation.</li> <li>Results show that long range correction for the L-J term is very important for the calculation of surface tension.</li> </ul>	Shi et al. (2006) [11]

Table 1. (Continued)

Table 1. Summary of investigations on interfacial phenomena in two phase flow. (Continued)

Nature of work	Features of MD Simulation	Observations and conclusions	Reference
Capillary waves at the liquid-vapor interface.	Potential: SPC/E Long range: PPPM $N = 1000$ , $\Delta t = 1$ fs, $r_c = 10 \text{ \AA}$ $T = 300\text{--}500\text{K}$	<ul style="list-style-type: none"> <li>Studied the effect of capillary wave at the liquid-vapor interface.</li> <li>Surface tension determined by pressure integration method at the interface was compared with a number of standard three point and four point models.</li> <li>All the models under-predict the experimental value, but SPC/E three point model and TIP4P-Ew four point model are significantly closer to the experimental value.</li> <li>Observed that <math>10 \text{ \AA}</math> L-J cut off with long range tail correction is sufficiently accurate for computing the surface tension.</li> <li>By using long simulation time and fine k space mesh, more accurate results could be obtained for SPC/E model.</li> </ul>	Ismail et al. (2006) [12]
Simulation of the liquid-vapor interface.	Potential: L-J $r_c = 2.5\sigma$ , $5.5\sigma$ & $6.5\sigma$ $T_r = 0.7, 0.85, 1.1$ .	<ul style="list-style-type: none"> <li>To study the Influence of cut-off radius on the interfacial properties, long range correction is applied to the dynamics and surface tension.</li> <li>Coexisting densities agree with NPT-test particle method, for large systems.</li> <li>Observed that a cut off radius of at least <math>5</math> molecular diameters with a tail correction is required to obtain reliable values for surface tension.</li> </ul>	Mecke et al. (1997) [13]
Molecular Dynamics of fluid phase change.	Potential: L-J	<ul style="list-style-type: none"> <li>Reviewed the Investigations done recently by the group on the evaporation-condensation of pure fluids under equilibrium and non equilibrium conditions and also the gas adsorption dynamics.</li> <li>Condensation coefficient under equilibrium condition is found to be species dependent and highly temperature dependant. This is explained from the view point of structure of the liquid surface and the molecular exchange.</li> <li>Under non equilibrium condition the condensation behavior strongly depend on the temperature and density of vapor.</li> </ul>	Matsumoto (1998) [29]
Condensation and evaporation coefficient.	Potential: L-J $N = 864$ , $1728$ , $T = 84\text{K--}130\text{K}$ $\Delta t = 5$ fs, $r_c = 3.5\sigma$ Integration: Verlet	<ul style="list-style-type: none"> <li>The effects of translational motion of molecules on the condensation and evaporation behavior are studied for an argon system.</li> <li>At elevated surface temperature both coefficients decrease due to increasing ability of reflection by the surface molecules.</li> <li>Velocity distributions of evaporated and reflected molecules are presented in the form of modified Maxwellian.</li> </ul>	Tsuruta et al. (1999) [14]

Properties at the liquid-vapor interface.	<p>Potentials: ST &amp; STS  <math>N = 2048</math>, <math>r_c = 2.5\sigma</math>,  <math>4.4\sigma</math>, <math>5.5\sigma</math>  <math>T_r = 0.7</math> &amp; <math>0.92</math>.</p>	<ul style="list-style-type: none"> <li>Performed canonical MD and MC simulations under the same setup conditions.</li> <li>Investigated the effect of cut off radius on the interfacial properties obtained by the simulation using ST and STS potential.</li> <li>MD and MC simulations give same results when the potentials used are same.</li> <li>To reproduce the full L-J potential critical parameters, a cut off radius of 5 to <math>5.5\sigma</math> is enough.</li> </ul>	Trokhymchuk & Alejandre (1999) [15]
Continuous liquid-vapor phase transition in microspace.	<p>Potential: L-J  <math>\Delta t = 10fs</math>, <math>N = 1000</math></p>	<ul style="list-style-type: none"> <li>Investigated the characteristics of liquid-vapor phase transition of argon fluid in microspace using MD/MC simulation.</li> <li>A gradual density variation across the interface was observed.</li> <li>Close to critical temperature, the interface thickness increases.</li> </ul>	Guo et al. (2000) [30]
Investigation of thickness effect on liquid films	<p>Potential: L-J  <math>r_c = 5.0\sigma</math>, <math>\Delta t = 5fs</math></p>	<ul style="list-style-type: none"> <li>Effect of film thickness on the interfacial properties was investigated.</li> <li>Surface tension values differ slightly with the change in film thickness.</li> <li>Developed a method to obtain accurate estimation of the local pressure distribution across the film.</li> <li>Observed that minimum thickness of a stable liquid film depends on both cross sectional area of the film and system temperature.</li> <li>Molecular distribution at different temperatures indicated that the interface behaves as a wave-like surface.</li> <li>As the film gets thinner, rupture may occur.</li> </ul>	Weng et al. (2000) [16]
Simulation of droplet evaporation.	<p>Potential: L-J, <math>r_c = 3\sigma</math>                      Integration: Gear's fifth order predictor corrector, Fluid: Xenon  <math>N = 205</math>, <math>783</math>, <math>2000</math></p>	<ul style="list-style-type: none"> <li>Vaporization characteristics of xenon submicron droplets in nitrogen ambient under subcritical and supercritical condition were investigated.</li> <li>Effect of system size, ambient and the droplet properties on droplet vaporization were examined.</li> <li>Observed that sphericity of droplet is maintained under subcritical condition and because of the reduction in surface tension, it deteriorates in the supercritical condition.</li> </ul>	Consolini et al. (2003) [31]

Table 1. (Continued)

Table 1. Summary of investigations on interfacial phenomena in two phase flow. (Continued)

Nature of work	Features of MD Simulation	Observations and conclusions	Reference
Condensation / evaporation at the interface of argon vapor and its condensed phase.	Potential: L-J (above triple point) Dymond-Alber potential (below triple point) Integration: leap frog method N = 2000, 4000 $\Delta t = 1$ fs, $r_c = 15 \text{ \AA}$ .	<ul style="list-style-type: none"> <li>Equilibrium simulation for the condensation/evaporation at the interface of vapor and its condensed phase and also simulation for evaporation into vacuum were done.</li> <li>Fitted density profiles for both cases agree with each other quantitatively and qualitatively.</li> <li>Condensation coefficients were plotted against temperature and compared with other models in the literature.</li> <li>Velocity distribution function of spontaneous evaporation is half Maxwellian at low temperatures and deviates from the half Maxwellian at high temperatures.</li> </ul>	Ishiyama et al. (2004) [17]
NEMD simulation to study evaporation/condensation process.	Potential: L-J N = 12000, $\Delta t = 1.19$ fs, $r_c = 4\sigma$ .	<ul style="list-style-type: none"> <li>Density, pressure and temperature were predicted using NEMD simulation.</li> <li>Predicted values of evaporating coefficient were compared with data from other equilibrium models in the literature and the transition state theory, a reasonable agreement was observed.</li> </ul>	Wang et al. (2005) [18]
Disjoining pressure effect in the thermodynamic equilibrium conditions at the interface of thin liquid films.	Potential: L-J $\Delta t = 5$ fs, $r_c = 5\sigma$ Ensemble: NVE+ $\mu$ PT	<ul style="list-style-type: none"> <li>A hybrid <math>\mu</math>PT simulation of argon thin film on solid surface was performed.</li> <li>Simulation predicts density and pressure variation in thin films as well as the equilibrium vapor pressure variation with respect to temperature and thickness of film.</li> <li>Predicted equilibrium vapor pressure values agree with conventional disjoining pressure theory.</li> <li>For very thin films on solid surface, predicted vapor pressure is found to drop well below the saturated value. This suggests the strong influence of disjoining pressure in thin films.</li> <li>Presence of a wall affected layer shows little effect on the vapor pressure.</li> </ul>	Carey and Wemhoff (2006) [19]
Diffusion at the liquid-vapor interface.	Potential: L-J N = 2592, $r_c = 3.02\sigma$ Ensemble: NVT (Nose Hoover)	<ul style="list-style-type: none"> <li>Molecular diffusion at liquid-surface was studied using intrinsic sampling method.</li> <li>Coefficient of diffusion parallel and perpendicular to the interface were studied for different system sizes and temperatures.</li> </ul>	Duque et al. (2008) [32]

	<ul style="list-style-type: none"> <li>• With increase in temperature, diffusion becomes faster and residence time shorter as expected.</li> <li>• Concluded that the turns over process by which a molecule enters and leaves the surface are as important as diffusion.</li> </ul>		
Influence of nano structured surface on the evaporation rate of ultra thin liquid film.	<ul style="list-style-type: none"> <li>• Evaporation rate of ultra thin liquid film on nano structured surface was found to be high compared to that on a flat surface, when the film thickness is larger than that of adsorbed layer.</li> <li>• This enhancement is due to a reduction in thermal resistance at the solid-liquid interface with increase in solid surface area.</li> </ul>	Argon: L-J Argon-Platinum: modified L-J $\Delta t = 5\text{fs}$ , $r_c = 3.5\sigma$	Nagayama et al. (2009) [33]
<b>Alcohols</b>			
Study of the structural and dynamic properties of liquid-vapor interface of methanol.	<ul style="list-style-type: none"> <li>• Procedure used in the analyses is almost same as that for water and L-J fluids.</li> <li>• Interfacial thickness for methanol is less than L-J at the lowest temperature.</li> <li>• The simulated thickness agrees well with thickness measured using ellipsometric technique.</li> <li>• Predicted surface tension is found to be lower than that of real methanol.</li> <li>• Orientation ordering of methanol is found to be much stronger than water.</li> <li>• Due to strong hydrogen bonding surface entropy is low for methanol and water than that of L-J fluids.</li> <li>• Surface potential is less than water.</li> <li>• Because of strong orientational tendency, surface potential remains non zero even at high temperatures.</li> </ul>	Potential: TIPS model, Long range: Edwald summation. $N = 1000$ $\Delta t = 0.7-0.85\text{fs}$ $T = 160-350\text{K}$ .	Matsumoto & Kataoka (1989) [20]
Many body interaction in liquid methanol.	<ul style="list-style-type: none"> <li>• Many body interactions are evaluated to accommodate the variation of dipole moment with respect to the environment like liquid, vapor and interface.</li> <li>• Predicted values of structural and thermodynamic properties, as well as surface tension are in good agreement with experimental values.</li> <li>• Dipole moment changes from 1.73D in gas phase to 2.81D in liquid phase. This shows the effect of many body interactions in methanol.</li> <li>• Diffusion coefficient agrees with experimental result.</li> </ul>	$N = 500$ , $r_c = 9\text{\AA}$ Ensemble: NPT+NV Constrain: SHAKE	Dang & Chang (2003) [21]

Table 1. (Continued)

Table 1. Summary of investigations on interfacial phenomena in two phase flow. (Continued)

Nature of work	Features of MD Simulation	Observations and conclusions	Reference
Study on the interfacial properties of ethanol.	Potential: OPLS/UA & OPLS/AA $\Delta t = 1$ fs, $r_c = 11$ Å Ensemble :- NPT+NVT	<ul style="list-style-type: none"> <li>Investigated the structural, thermodynamic and dynamic properties of liquid-vapor interface of ethanol.</li> <li>Temperature dependence of surface tension is correctly predicted by both potentials.</li> <li>In all the temperatures considered, interface thickness predicted by OPLS/UA is high.</li> <li>Interface thickness obtained by both potentials underestimate the experimental results.</li> <li>Diffusion coefficient was calculated.</li> <li>Of all the properties investigated, the results from OPLS/AA potential are found to be more close to actual values.</li> </ul>	Taylor & Shields (2003) [22]
<b>Mixtures</b>			
Liquid-vapor interface of methanol-water mixtures	Many body polarizable potential model $\Delta t = 2$ fs, $r_c = 9$ Å Ensemble: NVT Ion concentration: 0.05–0.95	<ul style="list-style-type: none"> <li>Investigated the structural, thermodynamic and electrostatic properties of the liquid-vapor interfaces of methanol-water mixtures of varying composition.</li> <li>Interface thickness was found to increase with increase in methanol concentration.</li> <li>Density profiles are quite smoother than water or methanol.</li> <li>Surface tension of the solution decreases with an increase in methanol concentration.</li> <li>The results on the radial distribution function (RDF) and the angular probability distributions provide information on the structure of methanol-water mixtures.</li> <li>Depending on the ion concentration, hydrogen bonding at the interface of methanol-water mixture changes.</li> <li>Dipole moment of methanol and water molecules at the interface approaches a value close to gas phase.</li> <li>Dipole moment of methanol in the mixture is more, compared to the bulk value.</li> </ul>	Chang & Dang (2005) [23]
Dynamics of water molecules at the liquid-vapor interface of aqueous ionic solutions.	Water: - Potentials: Water-SPC/E Sodium & chloride: L-J Long range: Ewald $\Delta t = 1$ fs, $T = 298$ K	<ul style="list-style-type: none"> <li>Dynamic properties of water molecules at the liquid-vapor interfaces of aqueous NaCl solution at varying ion concentration were studied.</li> <li>Density, surface tension and orientation profile at the interface were determined.</li> <li>With an increase in ion concentration, a decrease in interface thickness and increase in surface tension were observed.</li> <li>The rate of molecular relaxation increases with increase in ion concentration.</li> </ul>	Paul & Chandra (2003) [24]

Investigation on the structural and dynamic properties of the liquid-vapor interface of water-trimethylamine-N-oxide (TMAO) mixture of varying concentration.	Water :- Potential: SPC/E TMAO :-All atom model $\Delta t = 1$ fs, $T = 298$ K	<ul style="list-style-type: none"> <li>• Interfacial properties of water-TMAO mixture were calculated.</li> <li>• Water-TMAO hydrogen bond is found to be much stronger than water-water bond.</li> <li>• A decrease in surface tension with increase in TMAO concentration was observed.</li> <li>• As the TMAO concentration increases the number of ww (water-water) and wt (water-TMAO) hydrogen bonds decreases and that of wt/w (water-TMAO per water) increases.</li> <li>• Up to <math>x_{\text{TMAO}} = 0.5</math>, diffusion coefficient is found to decrease and then increase.</li> </ul>	Paul (2010) [34]
<b>Refrigerants and other fluids</b>			
Study on the vapor-liquid equilibrium of alternative refrigerants	Potential: 2CLJD	<ul style="list-style-type: none"> <li>• Vapor-liquid equilibrium data like coexisting densities and vapor pressure were calculated.</li> <li>• For all the refrigerants investigated, simulated liquid densities and vapor pressure are in good agreement with REFPROP values.</li> </ul>	Lisal et al. (1999) [25]
Liquid-vapor interfacial characteristics of R141b boiling flow in micro/nano channel.	Potential: 2CLJD $\Delta t = 5$ fs, for liquid $r_c = 3.17\sigma$ for vapor $r_c = 5.17\sigma$	<ul style="list-style-type: none"> <li>• NEMD Simulation was done on the interfacial properties of R141b, on the basis of an annular flow model.</li> <li>• Effect of varying saturation temperature of the system with different superheating at the bottom wall on temperature distribution, heat flux, density and interface thickness was studied.</li> </ul>	Dong et al. (2006) [26]
Interfacial properties of Dimethyl sulphoxide.	Potential:-A fully flexible nonpolarizable potential model $\Delta t = 2$ fs, $r_c = 9\text{\AA}$ Long range: Ewald sum Ensemble: NPT	<ul style="list-style-type: none"> <li>• Structural, thermodynamic and dynamic properties were analyzed for varying temperatures from 298 to 373 K.</li> <li>• Temperature dependence of interface thickness and self diffusion coefficient is found to be the same as for other fluids in the literature.</li> <li>• Surface tension decreases linearly with an increase in temperature and the simulation is found to under predict the experimental values.</li> <li>• Influence of Ewald sum and flexibility in the model were demonstrated.</li> </ul>	Senapathi (2002) [27]

Matsumoto and Kataoka [1] analyzed water and L-J fluids. The density profile was fitted using a hyperbolic tangential function. Predicted values of liquid density for water were found to be lower by about 15%–25% than that of real water. A decrease in the liquid density and an increase in the vapor density were observed with an increase in the temperature, as shown in Fig. 1 (a). The interface thickness was determined from the density profile. The distance over which the density changes from 10% to 90% of the bulk liquid value was considered to be the interface thickness. This concept has been generally followed in the literature. The thickness obtained from the simulated density profile ( $t_d$ ) was compared with the thickness obtained from an energy profile ( $t_u$ ) and that from ellipsometry measurement ( $t_{el}$ ). The values of  $t_d$  and  $t_u$  were found to agree well for water than the L-J fluid, whereas a large difference was noticed between  $t_d$  and  $t_{el}$  for water than the L-J fluid, as shown in Fig. 2 (a) and Fig. 5.

Townsend and Rice [2] predicted the interfacial thickness of water using spherically truncated (ST-2) and Lemberg- Stillinger-Rahman (LSR) potential models. The value of the thickness obtained from both models ( $3.45\text{\AA}$  at 300K) was found to be in good agreement with the value obtained using x-ray reflectivity technique ( $3.3\text{\AA}$ ). The density profile shows the same trend as obtained by Matsumoto and Kataoka [1]. Predicted result showed that the interfacial density distribution is less affected by the size of the system and the intermolecular potential. Maruyama et al. [3] simulated droplets of water and argon surrounded by their vapor. For water, the simulated liquid and vapor density values differed from the corresponding saturation values, but for L-J fluids like argon they were found to agree well, as shown in Fig. 1 (b) and Fig. 4 (b) respectively.

The interfacial thickness determined by Alejandre et al. [4] using extended simple point charge (SPC/E) interaction potential model for water was found to be lower than the experimental values [1] for varying temperatures, as seen in Fig. 2 (b). They claimed that this difference is due to the effect of capillary waves, which are absent in the simulation. Taylor et al. [5] compared the predicted thickness using the SPC/E model for water with measured thicknesses using ellipsometry and x-ray reflection, and also with the results of Matsumoto and Kataoka [1] using Carravetta-Clementi (CC) potential, as shown in Fig. 2(c). Both the potentials were found to underestimate the experimental values, which effect was attributed to the lack of considering capillary waves in the simulation. The density profile of Dang and Chang [7] using polarizable model for water, shown in Fig. 1 (e), is quite similar to that of Motakabbir and Berkowitz [6] and Taylor et al. [5], shown in Fig 1(d). Liquid density of  $0.99\text{g/cm}^3$  and an interfacial thickness of  $3.2\text{\AA}$  at 298K were obtained. As obvious, the liquid density obtained is very close to the bulk density.

A comparison of the coexisting densities evaluated using the self-consistent point dipole polarizability model (SCPDP) and SPC/E model [4] for water for a temperature range of 300–600K with experimental values was presented by Rivera et al. [8] as given in Fig. 3 (a). The comparison between the experimental values and the SPC/E model shows that the SPC/E model is in better agreement with experimental results. However, the interface thickness from the SCPDP model is in good agreement with experimental values [1] than the SPC/E model. Predicted values given by Yang and Pan [9] for the liquid and vapor densities of water, using the TIP4P model, agree fairly well with other models in the literature. Still, the model under-predicts the liquid density with respect to the tabulated data in the range 3% to 10% and the relative deviation for vapor density is much larger, as clear from Fig. 3 (b). This suggests the limitation of the TIP4P model. The interface thickness is found to vary from 4 to 8  $\text{\AA}$  within the temperature range of 300–480 K and is fitted very well with temperature, as given in Fig. 2 (d), in the following form:

$$t = -10.95 + 0.04068 T \quad (1)$$

The density profiles obtained from the simulation of a thin liquid film on a solid surface by Wemhoff and Carey [10] are qualitatively similar for both a non-polar liquid like nitrogen and a polar liquid like water. In addition to the bulk liquid, the interface, and the vapor regions, there is a wall affected region

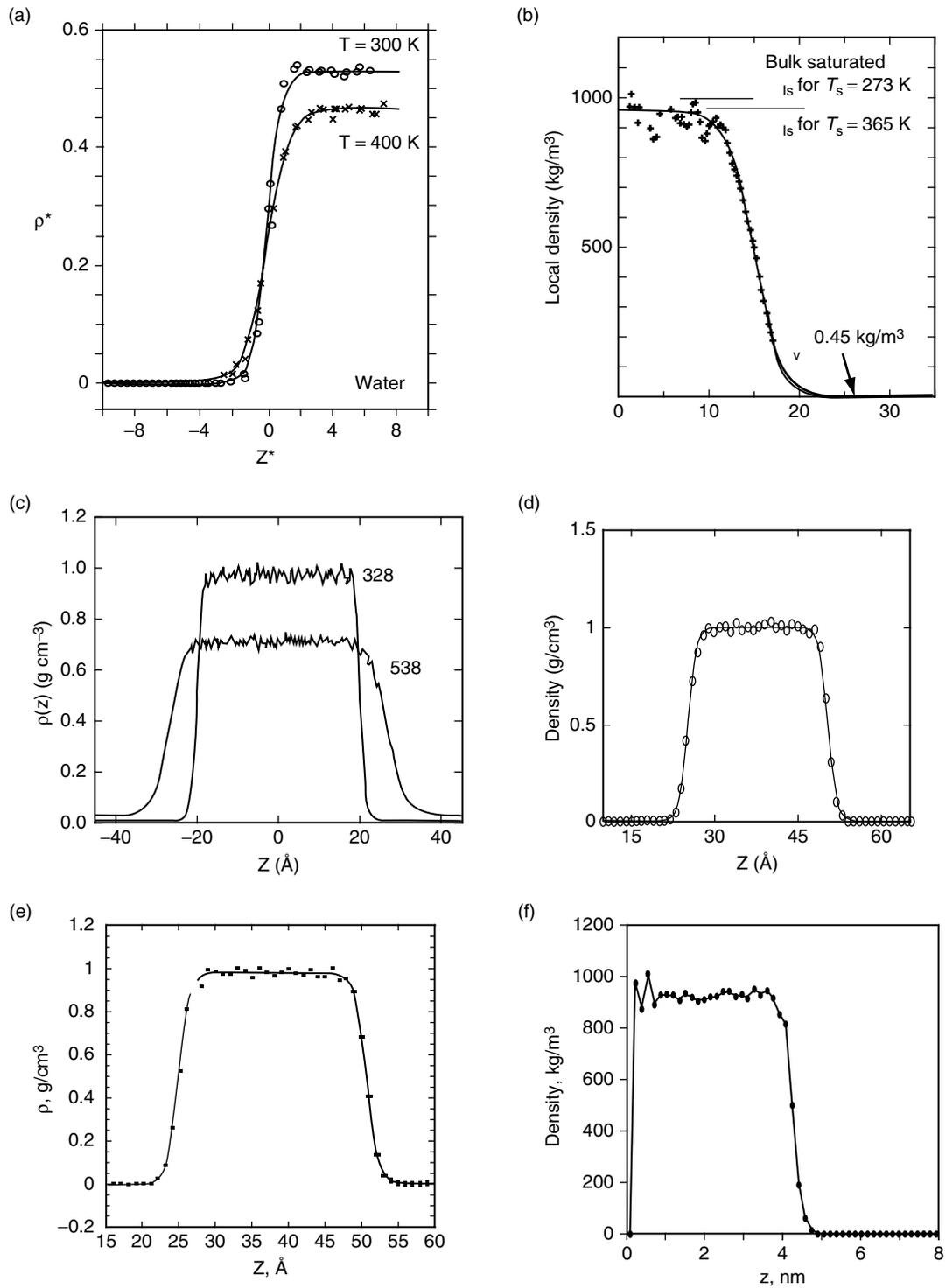


Figure 1. Density profile with a tangential fit from the studies of (a) Matsumoto et al. [1], (b) Maruyama et al. [3], (c) Alejandre et al. [4], (d) Taylor et al. [5], (e) Dang and Chang [7], (f) Wemhoff and Carey [10].

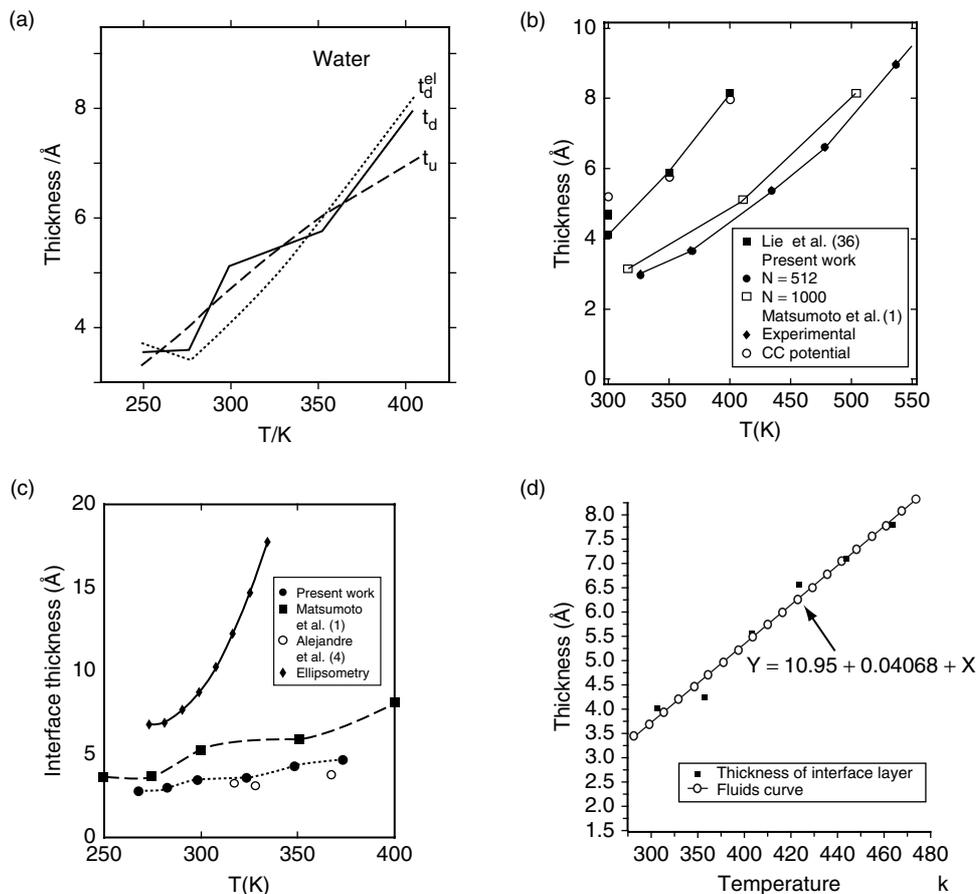


Figure 2. Variation of interface thickness with temperature for water from the studies of (a) Matsumoto and Kataoka [1], (b) Alejandre et al. [4], (c) Taylor et al. [5], (d) Yang and Pan [9].

also in the density profile, as inferred from Fig. 1 (f). The existence of the peak in the wall affected region of the density profile suggests an ordering of molecules near the surface. The bulk liquid density value calculated for nitrogen from its density profile for reduced temperature,  $T_r = 0.55$  is  $825 \text{ kg/m}^3$ , and this value agrees well with the ASHRAE recommended value of  $840 \text{ kg/m}^3$ . However, for water, the calculated bulk liquid density value tends to be slightly less than the ASHRAE value.

From the density profile fitted by Shi et al. [11] with the SPC/E model for water using particle-particle mesh method (PPPM) at 302 K, the interface thickness was calculated as  $3.91 \text{ \AA}$  and was found to be smaller than the experimental data [1]. At low temperatures, the density values agree well with the experiment than other models in the literature, but near the critical temperature, the calculated liquid density is found to be lower than the experimental value, whereas the vapor density is higher, as seen in Fig. 3(c). This shows the inaccuracy of the SPC/E model for the high temperature simulations. Ismail et al. [12] observed that fitting the density profile with the error function yields more accurate results than using a hyperbolic tangential fit. It was also observed that, if the effects of capillary waves at the interface are not taken in to account, the values of interfacial width and other properties will tend to be incorrect.

Mecke et al. [13] simulated the liquid-vapor interface for the pure L-J fluid. The system was simulated using different cut off radii, with and without a long range correction. A comparison of the result with the results of the NPT+ test particle method, which is known to yield very accurate results for these properties, showed that at low temperatures, a deviation of only 1% occurs for a cut off radius

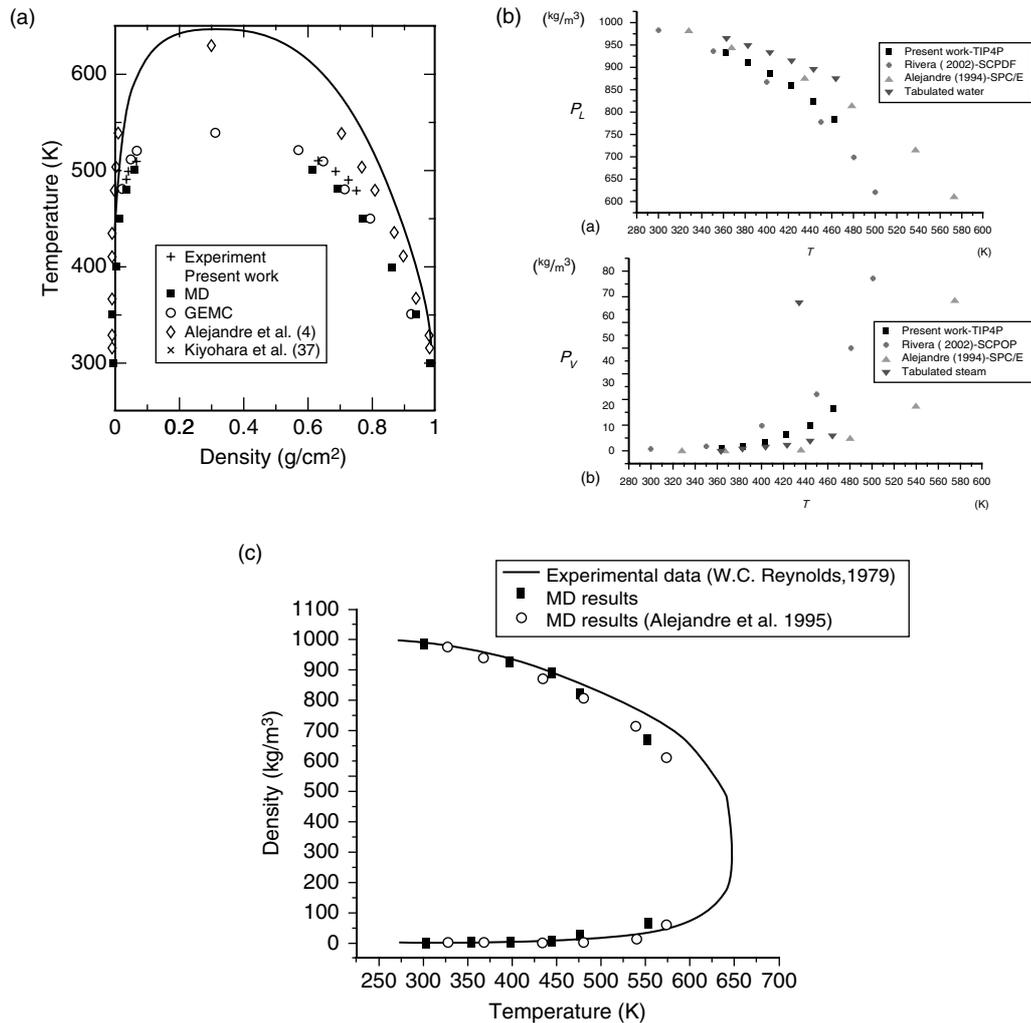


Figure 3. Liquid-vapor coexisting curves for water (a) Rivera et al. [8], (b) Yang and Pan [9], (c) Shi et al. [11].

of  $5.0\sigma$ , with a long range correction. The discrepancy occurring at high temperature could be reduced to 0.4%, by considering a larger system. Liquid densities obtained for varying temperatures in the simulation of argon by Tsuruta et al. [14] are close to the corresponding saturated values, as shown in Fig. 4(c). Trokhymchuk and Alejandre [15] investigated the liquid-vapor interface of Lennard–Jones fluids using the Monte Carlo Method (MC) and Molecular Dynamics (MD) with truncated potentials like spherically truncated (ST) and spherically truncated and shifted (STS) potentials. Density values obtained with ST and STS potentials were different at low cut-off radii. As the cut off radius was increased to  $5.5\sigma$ , this difference reduced, as both potentials approached the full L-J potential. Weng et al. [16] investigated the effect of the film thickness on the interfacial properties of L-J fluid. The liquid density and vapor density were found to be invariant with respect to the film thickness and were close to the bulk saturated densities. The density profiles fitted by Ishiyama et al. [17] for the simulation of liquid–vapor equilibrium and evaporation into vacuum are found to agree with each other, especially at low temperatures, as shown in Fig. 4(d).

The density profile obtained by Wang et al. [18] from the simulation of evaporation using Non-Equilibrium Molecular Dynamics (NEMD) shows the same trend as the equilibrium models in the

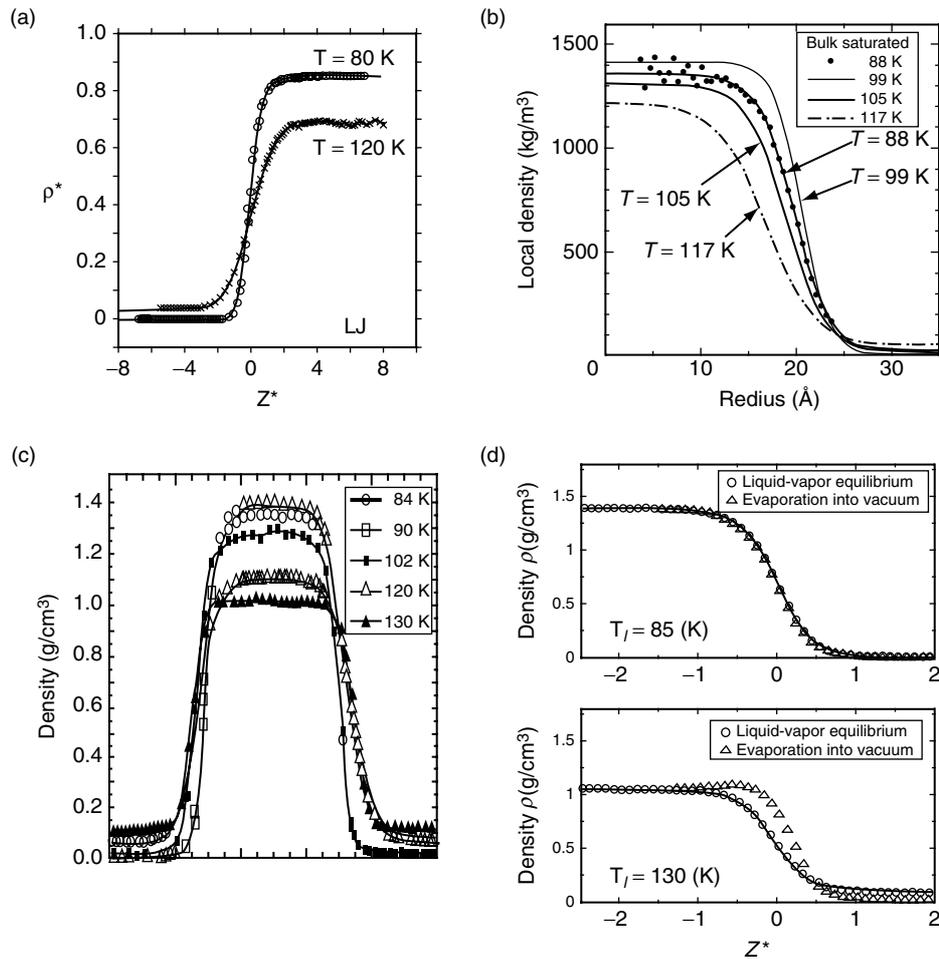


Figure 4. Density profiles for L-J fluids (a) Matsumoto & Kataoka [1], (b) Maruyama et al. [3], (c) Tsuruta et al. [14], (d) Ishiyama et al. [17].

literature. The density of the vapor is found to be increasing with time, as expected. Density profile obtained for the simulation of thin argon film on the solid surface by Carey and Wemhoff [19] shows a peak density in the wall-affected region and this peak diminishes away from the wall. Values of the bulk liquid density agree well with ASHRAE recommended values.

Matsumoto and Kataoka [20] investigated the interfacial properties of methanol using almost the same procedure as that of water and L-J fluids [1]. Simulated density values fitted well with  $\tanh$  function at any temperature. In comparison with L-J fluids and water, the relation between  $t_d$  and  $t_u$  shows an intermediate behavior, i.e.  $t_d \leq t_u$ . Density profile predicted by Dang and Chang [21] for methanol also fits well using  $\tanh$  function and the estimated liquid density of  $0.79 \text{ gm/cm}^3$  is very close to the bulk value at 298 K. The calculated value of interface width at 298K was  $4.6 \text{ \AA}$ .

Taylor and Shields [22] simulated the liquid-vapor interface of ethanol using united-atom and all-atom optimized potential models for liquid simulations (OPLS/UA & OPLS/AA). Temperature dependence of the interface thickness and bulk density showed similar trend as other fluids. The density values obtained using the OPLS/AA potential was found to be more close to experimental values. Experimental value of the interface thickness obtained as  $17.7 \text{ \AA}$  was much larger than simulated values, which suggests the absence of the capillary wave effect in the simulation.

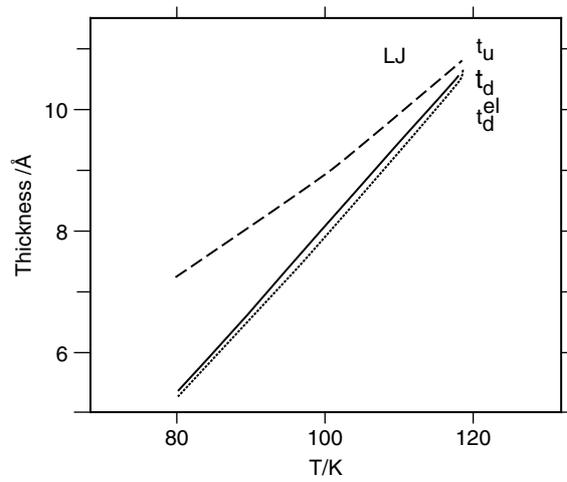


Figure 5. Interface thickness for L-J fluids: Matsumoto and Kataoka [1].

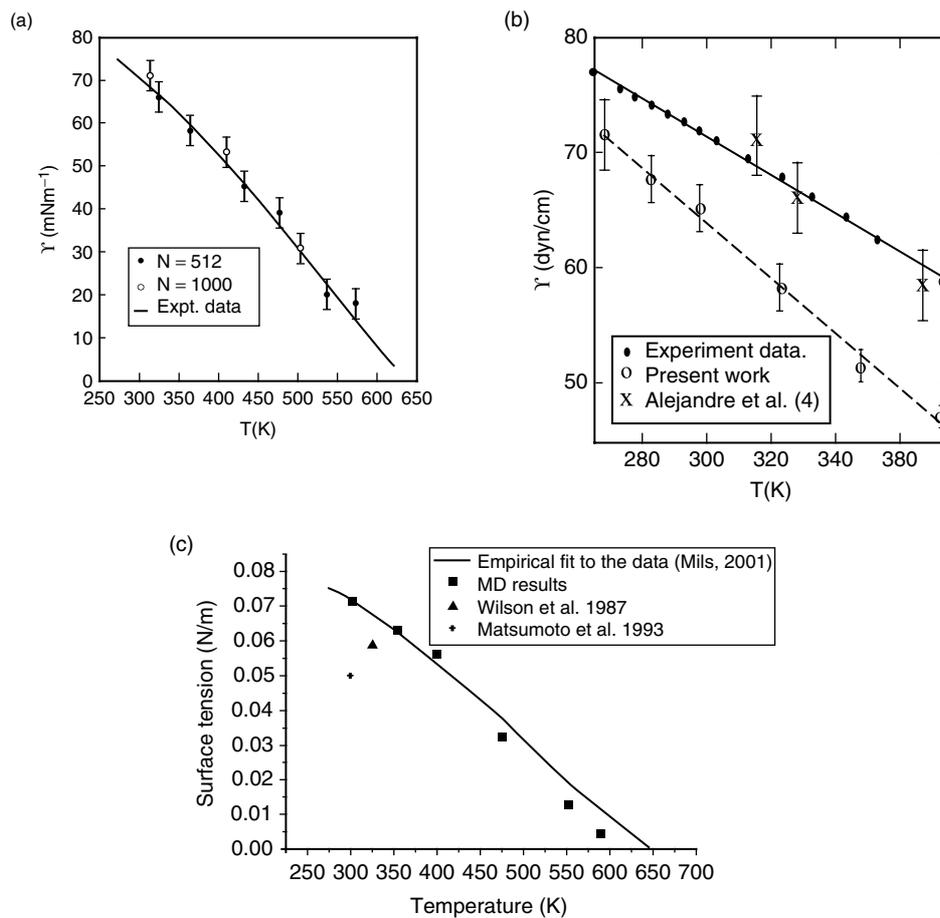


Figure 6. Variation of surface tension with temperature for water from the studies of (a) Alexandre et al. [4], (b) Taylor et al. [5], (c) Shi et al. [11].

Chang and Dang [23] studied the interfacial phenomena of methanol-water mixture for varying composition. The density profile for the mixture is found to be quite smooth than water or methanol. The interface thickness is observed to be increasing with increase in methanol concentration. Paul and Chandra [24] simulated the liquid-vapor interface of pure water and aqueous NaCl solution of different concentration. Density profile obtained shows the same trend as other fluids. Thickness of the interface found to decrease with increase in ion concentration.

Lisal et al. [25] studied the vapor-liquid equilibrium of alternative refrigerants using Two-Centre Lennard-Jones Potential with a point dipole (2CLJD) model. The saturated densities obtained are found to be in good agreement with REFPROP values. Dong et al. [26] simulated the interfacial phenomena for the refrigerant R141b in micro/nano channel for different saturation temperatures and also for different degree of superheat. The obtained density profile shows an increase in the interface thickness, with increase in saturation temperature and also with increase in degree of super heat.

Senapathi [27] investigated the interfacial phenomena of dimethyl sulphoxide (DMSO) using a flexible, nonpolarizable potential model. The temperature dependence of density profile, bulk densities and interface thickness shows same trend as other fluids in the literature. The agreement between the simulated values and the experimental results suggests that the model successfully describes the interface.

## 2.2. Surface tension

Surface tension is frequently considered to validate the potentials and the types of interactions used in the Molecular Dynamic analysis of interfaces. Surface tension is usually determined by integrating the difference between the normal pressure and the tangential pressure across the interface. Matsumoto and Kataoka [1] compared their result for surface tension, obtained from an analysis of water, using the CC potential, with experiment and found that the simulated value is only half of the experimental value. Maruyama et al. [3] used the Laplace-Young equation to determine the surface tension of a liquid droplet of argon surrounded by its vapor. In order to find the normal pressure distribution, the spherical extension of Irvin-Kirkwood formula was used. The calculated values of vapor pressure and surface tension were plotted against temperature and the simulated values were found to be matching fairly well with the bulk value as given in Fig. 7 (a). A further analysis of the droplet size effect was also suggested.

Alejandre et al. [4] calculated the surface tension values for water with SPC/E potential with Ewald sum for long range correction. The simulated values were found to decrease with an increase in temperature, and were found to be in good agreement with experimental values as shown in Fig. 6 (a). Taylor et al. [5] calculated the surface tension of water using the theory of Kirkwood and Buff with SPC/E potential. The predicted results were compared with data from experiments and also with the

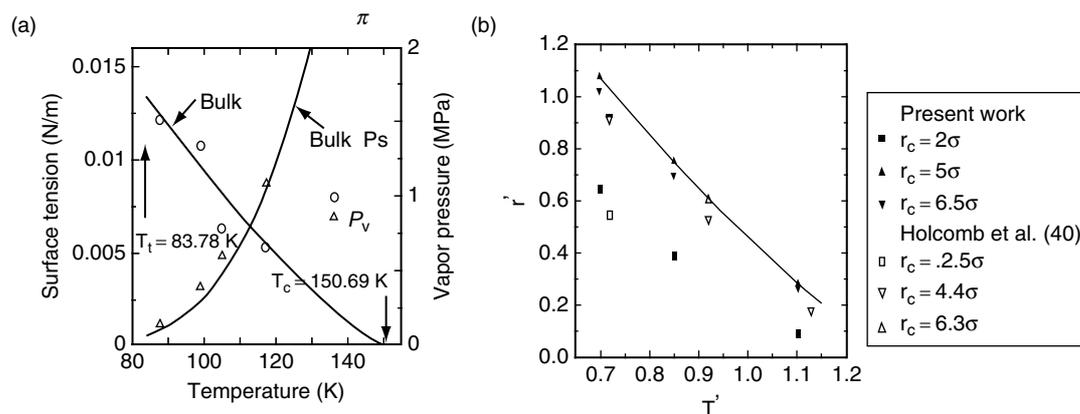


Figure 7. Variation of surface tension with temperature for L-J fluids: (a) Maruyama et al. [3], (b) Mecke et al. [13].

results from Alejandre et al. [4], who performed the simulation under similar condition, but had included the long range interaction. It was observed that by using the long range interaction, results of Alejandre et al. showed excellent agreement with experimental data as shown in Fig. 6 (b). To examine the quality of the developed polarizable potential model for water, Dang and Chang [7] calculated the surface tension at the liquid-vapor interface. A value of 92 dynes/cm was obtained, which is in reasonably good agreement with the experimental value of 72 dynes/cm. Rivera et al. [8] compared the surface tension values obtained for water with SCPDP model, with data from experiments and with the results of Alejandre et al. [4]. Results of Alejandre et al. found to agree better with the experimental values than the SCPDP model. It is also found that their result shows better agreement with experimental result while plotted against reduced temperatures, especially at higher values.

Shi et al. [11] determined the surface tension of the liquid-vapor interface of water using SPC/E potential with PPPM for long range interaction, and compared the results with thermodynamic correlations based on the equation of corresponding states for the surface tension of water. The result is shown in Fig. 6 (c). Simulation results agree very well with thermodynamic correlations especially at low temperatures. This agreement shows that long range interaction is to be considered during the calculation of surface tension. At high temperatures, because of the decrease in liquid density and increase in vapor density, the calculated value of surface tension is found to be different from the experimental value. Another reason pointed out for this disagreement is that the two interfaces of the interfacial film may not be independent due to long range interaction. So a thicker film was suggested for performing the simulation. Ismail et al. [12] compared the surface tension of water simulated using SPC/E potential with other three- point models including SPC/E models of Alejandre et al. [4] and Shi et al. [11], and also with other four-point models in the literature. The results from Alejandre et al. and Shi et al. were found to show better agreement with experimental data than any other models.

Mecke et al. [13] observed that by using a cut-off radius of at least  $5\sigma$  and with a tail correction, the surface tension values of L-J fluids will tend to a theoretical value of full L-J potential, as shown in Fig. 7(b). Trokhymchuk and Alejandre [17] noticed that surface tension values of L-J fluids, estimated by using ST and STS truncated potentials converge to full Lennard -Jones results by employing a cut-off radius of  $5.5\sigma$ . Weng et al. [16] observed that for a particular temperature, surface tension varies only slightly with varying film thickness and the average value is 0.78 at a reduced temperature of 0.818. The obtained value is found to be matching with the result of Mecke et al. [13].

Matsumoto and Kataoka [20] observed that the calculated surface tension values for methanol are 20%–30% less than that of real methanol. At the same time, Dang and Chang [21] noted that the predicted value of surface tension is 25 dynes/cm for methanol, and is found to agree with the experimental value of 23 dynes/cm. Simulation was found to under predict the value of surface tension for ethanol, as observed by Taylor and Shields [22].

Surface tension values calculated for methanol-water mixture [23] are found to decrease with increase in concentration and also agree with experimental results. For aqueous NaCl solutions [24], the surface tension is observed to increase with increase in ion concentration and is in good agreement with experimental results. Paul [34] investigated the interfacial properties of water-trimethylamine-N-oxide (TMAO) mixture for varying TMAO concentrations ( $x_{\text{tmao}}$ ). The calculated value of surface tension was found to decrease with an increase in  $x_{\text{tmao}}$  and further, this decrease was found to be more rapid after  $X_{\text{tmao}} = 0.5$ .

The predicted results of Dong et al. [26] for refrigerant R141b show a large fluctuation in the surface tension across the interface. A decrease in surface tension with an increase in saturation temperature and degree of superheat was also observed. A linear decrease in the surface tension with an increase in temperature was observed in the case of DMSO [27].

### 2.3. Pressure and temperature

Only very few investigations are available in the literature that predict the pressure and temperature distributions at the interface. Trokhymchuk and Alejandre [15] studied the effect of cut off radius on the pressure-temperature coexisting curves of L-J fluids using ST and STS truncated potentials. As in

the case of density, for a cut off radius of  $5.5\sigma$ , both models approached the full L-J potential. An improved method developed for pressure calculation by Weng et al. [16] showed less fluctuation in the predicted pressure distribution across the interface than the usual method. Pressure was found to decrease gradually from the liquid to the vapor region across the interface in the NEMD simulation by Wang et al. [18]. Carey and Wemhoff [19] predicted the equilibrium vapor pressure for a thin liquid film on a solid surface, which was plotted against thickness of the film. A reduction in predicted vapor pressure from the saturated value, for a film thickness of less than 1.5nm at the reduced temperature  $T_r = 0.6$  indicates the influence of solid-liquid intermolecular attraction, and there by suggests that the disjoining pressure is to be considered in the modeling of thin film transport. The vapor pressure values predicted by Lisal et al. [25] for different alternative refrigerants agree well with REFPROP.

Guo et al. [30] observed a monotonically varying temperature distribution across the liquid-vapor interface and also noted that the temperature at the interface is higher than the saturation temperature. Wang et al. [18] also have observed in their simulations that the temperature increases gradually from vapor to liquid region across the interface. A significant fluctuation in the local temperature values across the interface was observed in the simulation of R141b by Dong et al. [26].

#### 2.4. Diffusion coefficient

Molecular Dynamics simulations, among other discrete computational methods, have been used to predict the diffusion coefficient in some investigations. Townsend and Rice [2] observed that the diffusion coefficient for water at the interface is 58% higher than in the bulk liquid region. Taylor et al. [5] calculated the self diffusion coefficient of water molecules at the surface and in the bulk, using Einstein relation for varying temperatures. Diffusion was found to be faster at the surface than in the bulk. Simulated value for bulk liquid was found to agree fairly well with the experimental data as shown in Fig. 8(a). Dang and Chang [7] calculated the diffusion coefficient for bulk water as  $2.1 \times 10^{-5} \text{ cm}^2/\text{sec}$ , which value agrees well with the experimental result of  $2.3 \times 10^{-5} \text{ cm}^2/\text{sec}$  at 295K. Liu et al. [28] developed a method to determine the self diffusion coefficient in a finite region. They calculated the variation of the diffusion coefficient with respect to distance from the interface of water. Away from the interface the value was obtained as  $D \approx 0.22 \text{ \AA}^2/\text{ps}$ , which is in agreement with experimental bulk value. They suggested that the difference in the bulk and interfacial value is because of the existence of a fewer number of hydrogen bonds at the interface. At the interface, the diffusion coefficient was found to be anisotropic with values of the perpendicular and parallel components being  $D_{\perp} \approx 0.5 \text{ \AA}^2/\text{ps}$  and  $D_{\parallel} \approx 0.8 \text{ \AA}^2/\text{ps}$ , respectively.

Duque et al. [32] predicted the diffusion coefficient at the liquid-vapor interface of L-J fluids using intrinsic sampling method at different temperatures. Parallel diffusion coefficient at the reduced temperatures  $T^* = (k_B T/\epsilon) = 0.848 - 0.212$ , was observed to be almost 2–4 times larger than the bulk value, depending on the temperature. Perpendicular diffusion coefficient was found to be less than that of the parallel component, but more than the bulk value.

Dang and Chang [21] computed the self diffusion coefficient for methanol using mean square displacement method. The simulated value was found to agree with the experimental value. Self diffusion coefficient predicted by Taylor and Shield [22] for ethanol is found to be high at the surface than in the bulk fluid and is found to increase with an increase in temperature, as shown in Fig. 8 (b). Self diffusion coefficients for both water and TMAO were found to decrease with an increase in  $x_{\text{tmao}}$  up to  $x_{\text{tmao}} = 0.5$  and then increase, according to the investigation by Paul [34].

Senapathi [27] calculated the self diffusion coefficient of dimethyl sulfoxide (DMSO) from the velocity auto correlation function. The calculated value at the interface, as shown in Fig. 8(c), was found to be more than in the bulk value. The value was also found to increase with an increase in temperature as in the case of water [2, 5]. The simulated values of the self diffusion coefficient for bulk DMSO liquid was found to agree well with available experimental results.

#### 2.5. Condensation and evaporation coefficients

To determine the net condensation or evaporation rate during phase change, an accurate evaluation of

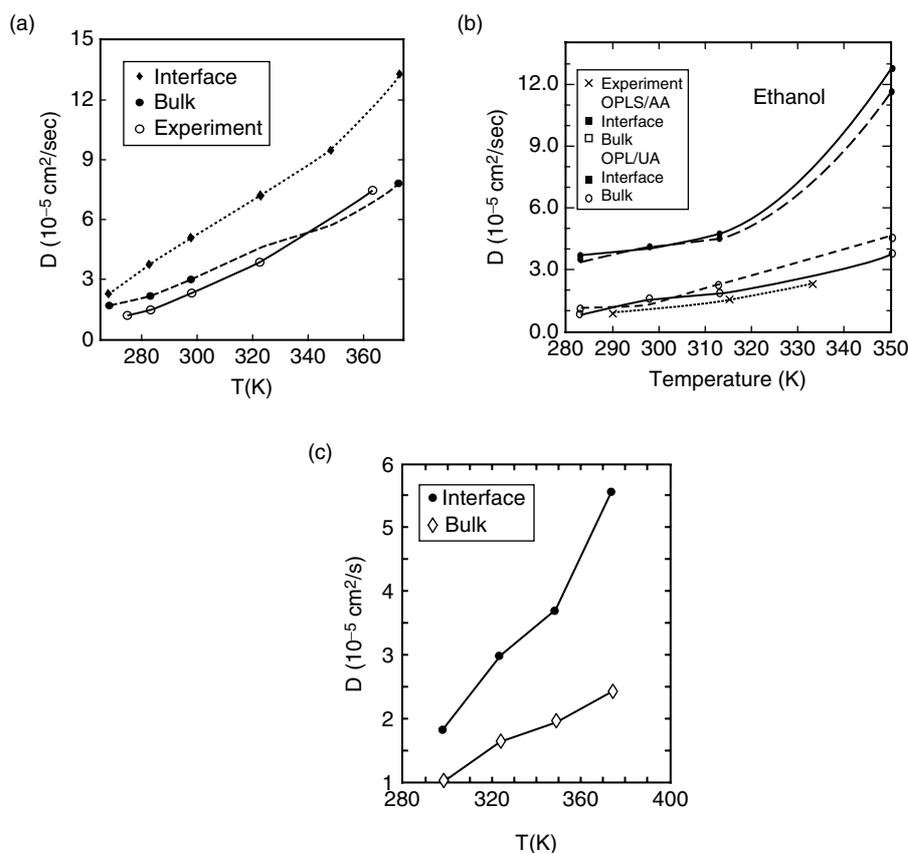


Figure 8. Self diffusion coefficient as a function of temperature: a) Taylor et al. [5], (b) Taylor & Shields [22], (c) Senapathi [27].

the condensation or evaporation coefficient is required. A Molecular Dynamics analysis of condensation or evaporation coefficient would be very much useful for this purpose. Condensation coefficient is defined as the fraction of incident molecules which condense on the liquid surface, while the evaporation coefficient is the fraction of molecules leaving the surface which get converted to vapor.

Yang and Pan [9] observed that the effect of the hydrogen bond due to the polar structure of water may recapture the molecules just evaporated and tend to reduce the evaporation coefficient. This effect is found to be dominant at low temperatures. It was also observed that, with an increase in the pressure, the evaporation coefficient increases. Matsumoto [29] investigated the dynamic behavior of molecules during condensation and evaporation. It was observed that due to molecular exchange, which does not contribute to condensation, the condensation coefficient is much less than unity for associating fluids like argon, water, etc. It was also concluded that the condensation coefficient is strongly dependent on the temperature, even for simple fluids as shown in Fig. 9(a).

Tsuruta et al. [14] conducted an analysis of argon molecules to investigate the effects of translational motion of mono-atomic molecules on condensation and evaporation coefficients. It was observed that both the coefficients increase with the normal component of translational energy and decreases with an increase of system temperature. Ishiyama et al. [17] determined the condensation/evaporation coefficient for argon liquid in vacuum. The predicted value was found to be close to unity below triple point and it was found to decrease with an increase in temperature. The values were compared with other models in the literature, as shown in Fig 9(b). Evaporation coefficients calculated by Wang et al. [18] using NEMD simulation were found to agree with data from transition state theory and also from

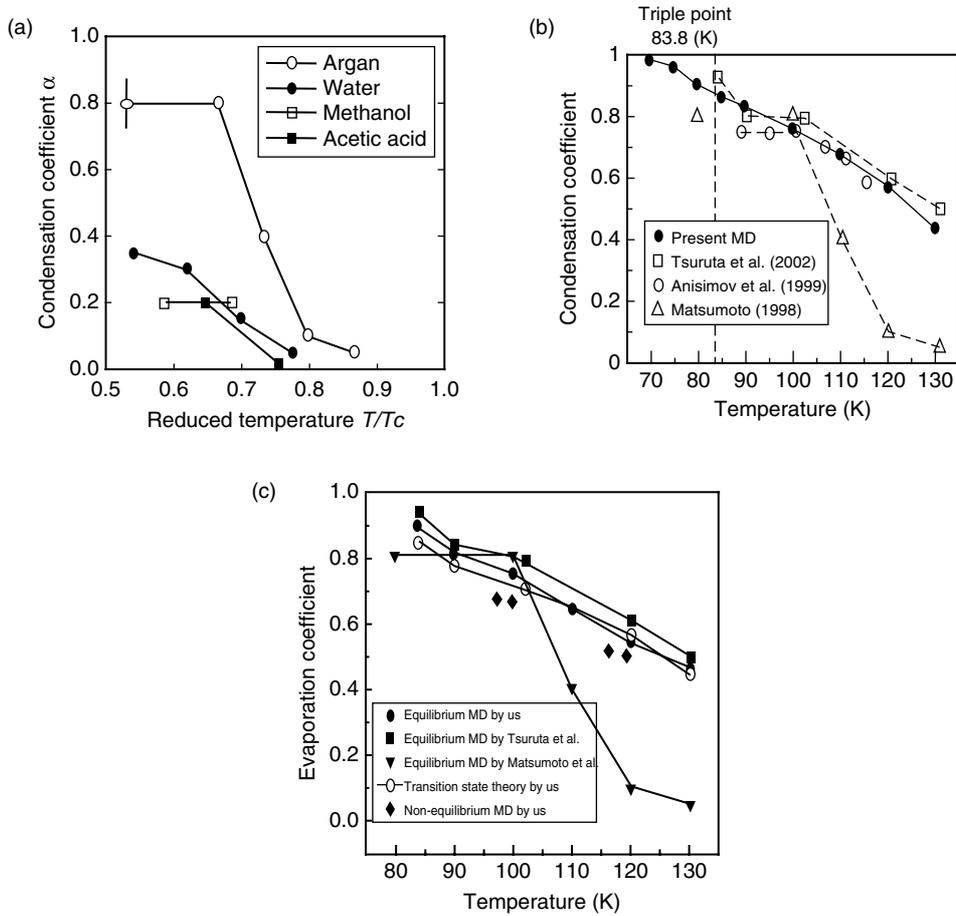


Figure 9. Variation of condensation/evaporation coefficient with temperature: (a) Matsumoto [29], (b) Ishiyama et al. [17], (c) Wang et al. [18].

other equilibrium models in the literature. However, the same results show large deviations compared to the data from Matsumoto et al. [38], especially at high temperatures, as seen in Fig. 9(c).

## 2.6. Structural orientation

Orientation distribution of water molecules at the liquid-vapor interface plays a large role in determining the reactivity of the interface. Some important investigations have been undertaken in this area. Matsumoto and Kataoka [1] studied the orientation ordering of water molecules near the interface using the CC potential. Two types of orientations were observed - in the vapor side, one hydrogen atom of a water molecule projects towards the vapor and in the liquid side, a molecule tends to lie down on the surface with both hydrogen atoms slightly directed towards the liquid. For water, this orientational tendency is found to be reduced at high temperatures. Taylor et al. [5] also observed two distinct orientations of water molecules at the interface, with the dipole of the water molecule at the vapor side directed out of the liquid at an angle of  $74^\circ$ , and on the liquid side, with the dipole lying in the plane of the surface with both hydrogen atoms pointing slightly towards the liquid. Matsumoto and Kataoka [20] have suggested that the orientation ordering of methanol is much stronger than water as it is having a hydrophobic methyl group projecting from the vapor to the liquid phase. Ordering is found to exist for methanol even at high temperatures.

Chang and Dang [23] observed that the surface structure of methanol-water mixture becomes less ordered with an increase in the methanol concentration. Hydrogen bonding at the interface was found to increase with an increase in the methanol concentration. The dipole moment of methanol molecules was found to become larger in the mixture, compared to the bulk value. Paul [34] observed that the dipole vector of interfacial water molecule changes with a change in the TMAO concentration and that this vector orients itself to maximize the hydrogen bonds.

### 3. CONCLUSIONS

Molecular Dynamics Simulations provide a reliable methodology to analyze interfacial phenomena and predict relevant properties at the interface in two-phase flow systems. Considerable amount of research efforts have gone into the fundamental problem, which will lead to applications in systems, especially those require accurate design procedures, such as micro and nanoscale systems utilizing phase change heat transfer. A detailed review of the results obtained during the Molecular Dynamics simulation of interfacial phenomena for the two phase flow reveal that properties such as the density, interface thickness, surface tension, pressure, temperature, diffusion coefficient, condensation/evaporation coefficient and structural orientations have been predicted using the simulation method, for different fluids.

The most important parameter that is found to cause deviations and variations among the results from various investigations is the choice of the potential function used in the analysis. For instance, in the case of water, the results obtained using an SPC/E model with long range correction is found to be more close to experimental results than those obtained using other potential models. When a fluid can be approximated as a Lennard-Jones fluid, application of the L-J potential with a cut off radius of  $5\sigma$  is recommended. The density profiles obtained for all fluids studied, irrespective of the potential function and the temperature selected, show qualitative agreement. It is found that these could be fitted fairly well using *tanh* function. In the case of water, an interface thickness of the order of 4–9 Å in the temperature range of 300–500K has been observed in the simulation results, whereas the experimental values are found to be more than this in most of the cases. A suggestion from the literature is that the capillary wave effect which is absent in simulations has also to be considered for obtaining an accurate value of the interface thickness. For the L-J fluid, a higher value of interfacial thickness than water has been observed. Irrespective of the method of calculation and the potential used, the diffusion coefficient determined has been found to be high at the interface than in the bulk fluid.

Only very few investigations deal with the simulation of the temperature and pressure variation across the interface. The importance of disjoining pressure, which occurs in thin films in contact with solid walls, has generally been investigated only for L-J fluids. Such studies could be extended to realistic fluids with appropriate potential functions, relating them to practical applications. It is also to be noted that analyses, in most of the cases, have been performed only for the basic geometry of the liquid slab. Extension of the methodology to domains with other interfacial geometries would provide interesting results in the analysis of evaporation and condensation systems in space applications or rarefied flow situations.

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