MD simulations of He evaporating from dodecane

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The velocity distribution of He atoms evaporating from a slab of liquid dodecane has been simulated. The distribution composed of ~10,000 He trajectories is shifted to fractionally faster velocities as compared to a Maxwell-Boltzmann distribution at the temperature of the liquid dodecane with an average translational energy of $1.05 \times 2RT$ (or $1.08 \times 2RT$ after correction for a cylindrical liquid jet), compared to the experimental work by Nathanson and co-workers ($1.14 \times 2RT$) on liquid jets. Analysis of the trajectories allows us to infer mechanistic information about the modes of evaporation, and their contribution to the overall velocity distribution.

Keywords: molecular dynamics, liquid jet, dodecane, evaporation

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1. Introduction

Gas-liquid interfaces are ubiquitous with almost three quarter of the earth's surface covered by water. In addition, aerosol particles have a large liquid surface area, both in relation to their own weight, and when the surface area of all atmospheric aerosol particles is combined,[1] and the chemistry of aerosols hence impacts many atmospheric processes.[2] Despite their obvious importance, liquid surfaces are less-well understood than solid surfaces, mainly due to the complexity that comes with the constantly changing molecular structure of the liquid surface.[3] Evaporation from liquids, be it the molecules that make up the liquid or species dissolved in it, is important in processes such as distillation and aspiration, but the mode of evaporation is not yet fully understood.[4] In this letter, we report molecular dynamics (MD) simulations of the evaporation of He atoms from liquid dodecane, $C_{12}H_{26}$.

Dodecane is a common solvent and the major constituent of kerosene,[5] which itself finds use as the organic phase in solvent extraction processes such as the PUREX process,[6] or as a fuel in aviation; $C_{12}H_{26}$ is in fact often used as a surrogate for kerosene in modelling. In this work, however, we report MD simulations which we performed to establish the kinetic energy distribution of evaporating atoms,[7] and which can be directly compared with recent experimental work by Nathanson and co-workers who studied the evaporation of He atoms from dodecane in a liquid jet.[8] Using a mass-spectrometer mounted in the plane perpendicular to a liquid jet in vacuum, they measured by means of time-of-flight methods the velocity distribution of He atoms which are initially dissolved in the dodecane liquid but evaporate when the liquid jet travels through vacuum. Their main result is that these He atoms do not exhibit a velocity distribution that matches a Maxwell-Boltzmann distribution of He atoms at the temperature of the liquid jet, but are slightly faster, with the He atoms having an average kinetic energy of $\sim 1.14 \times 2RT$.

The development of liquid jets can be mainly attributed to Faubel's work in the late-80s.[9,10] The group studied – amongst other phenomena – the evaporation of neat liquid jets; molecules from within these tend to evaporate with a thermal velocity distribution; however, there is no *a priori* reason as to why translational energy distributions of evaporating atoms or molecules should always follow a thermal Maxwell-Boltzmann translational energy distribution,[11] as Maxwell-Boltzmann distributions have been developed for a thermal ensemble of gas-phase particles at distances far away (further than the mean free path) from any surfaces or interfaces; furthermore, evaporation from a liquid in vacuum is not a process in equilibrium as the evaporated atoms are not condensing back into the liquid. Distributions which are non-Maxwellian in their translational and/or internal energy have in fact previously been observed for atoms or molecules desorbing from both liquid as well as solid surfaces.[10,12] According to the principle of detailed balance,[13] the kinetic energy distribution established in this work for He atoms evaporating from the liquid should be the same as the probability for a He atom at a given kinetic energy to be absorbed by the liquid dodecane;[14] if there is e.g. a small barrier for evaporation, then slow He atoms may not be able to escape the

liquid, and equally an incoming He atom with a low kinetic energy may not be able to overcome this barrier and may be reflected.[7,15]
The MD simulations described here record a flux of atoms as they cross an arbitrary plane above the liquid surface, and the atoms are recorded with equal probability independent of their velocity. The Maxwell-Boltzmann distributions for particles originating from a flat surface and being detected when traversing a parallel plane above are described by equation 1:[16]

$$P(v)\mathrm{d}v = \frac{1}{2}\left(\frac{m}{kT}\right)^2 v^3 \exp\left(-\frac{mv^2}{2kT}\right)\mathrm{d}v$$

Eqn. 1

The average translational energy of this normalized distribution is $2kT$.[16]
While much work has been done to study the structure and surface properties of liquid interfaces (described by Knudsen zones and capillary waves), and MD simulations have been used to investigate the structure of liquid interfaces, this work focussed on the molecular level description of the dynamics of evaporation of He atoms from liquid dodecane, a relatively simple system as He – being atomic – lacks the rotational and vibrational degrees of freedom that can add complexity;[17] these simulations are directly relevant to recent experimental studies on the evaporation of atoms and small molecules from liquids.[8]

2. Methods

The molecular dynamics simulations of dodecane described here were performed using the AMBER force field.[18] As a general purpose force field, AMBER has successfully been used for modelling liquids, and also well reproduced the bulk density of our liquid when compared to other force fields. We employed the all-atom 1995 release which includes harmonic bond and angle potentials for hydrocarbons; we felt it was necessary to include all atoms as they may have an effect on the helium atom velocities when e.g. a helium atom undergoes a final collision with a hydrogen atom of a dodecane molecule at the interface before evaporation, which would not be captured by a united-atom force field. AMBER does not, however, provide parameters for non-bonded interactions with neutral He atoms, hence values for these were taken from the United Force Field (UFF).[19] The non-bonding interaction between atoms of different dodecane molecules, atoms in the same molecule separated by more than three bonds (i.e. whose interaction is not governed by bond distance, angular, or torsional potentials), or between helium atoms and atoms in dodecane molecules is described by Lennard-Jones 12-6 potentials of the form

$$U(r_{ij}) = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]$$

Eqn. 2

where r_{ij} is the distance, σ_{ij} the Lennard-Jones contact distance, and ϵ_{ij} is the well-depth, all given in Table I. For interactions between unlike atoms, Lorentz-Berthelot combining rules apply:

$$\sigma_{ij} = \frac{1}{2}(\sigma_{ii} + \sigma_{jj})$$

Eqn. 3

$$\epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}}$$

Eqn. 4

Interatomic forces are truncated after 12 Å.

The C–C bond lengths as well as the C–C–C bond angles are described by harmonic potentials of the form

$$U(r) = \frac{1}{2}k_r(r - r_{eq})^2$$

Eqn. 5

and

$$U(\theta) = \frac{1}{2}k_\theta(\theta - \theta_{eq})^2$$

Eqn. 6

where k is the force constant for bond stretching and bending, respectively, and r_{eq} and θ_{eq} are the equilibrium bond distance and angle; their values are given in Table I. The torsional potential is described by

$$U(\phi) = A[1 + \cos(m\phi - \delta)]$$

Eqn. 7

where ϕ is the dihedral angle, and constants A, m, and δ are also given in Table I.

All simulations were performed in the *NVT* ensemble using the molecular dynamics program DL_POLY 4.03.[20] The temperature was regulated to 298 K by a Nosé–Hoover thermostat with a relaxation constant of 1 ps,[21] and the thermostat acted on all atoms including the He atoms once added. As is shown below in Fig. 3, the actual process of a He atom detaching itself from the surface takes less than 1 ps such that the relaxation constant is not expected to significantly influence the outcome of the simulations.

Simulations were started by placing 297 linear dodecane molecules (11286 atoms) into a simulation box of dimensions 53.2962 × 45.2441 × 44.5941 Å^3 ($x \times y \times z$) chosen to match the experimentally determined density of 746.0 g L^{-1}.[22] The z-dimension was then stretched to three times its original value (133.7823 Å) in order to create two liquid-vacuum interfaces with the liquid slab sitting in the centre and occupying one third of the volume. Periodic boundary conditions (PBC) were applied in all three dimensions such that molecules in the

top or bottom (vacuum) volume leaving the simulation box along *z* are re-captured; in the *x* and *y* direction, the PBCs cause a continuous liquid layer to be formed.[23]
The molecular dynamics simulations were run with a timestep of 1 fs (data printed every 100 steps), and after a relaxation period and once the configurational energy, E_{config}, has levelled off, Helium atoms were placed within the liquid slab. Almost 1000 different pure dodecane configurations were randomly selected, and grid searches were performed to identify pockets within the liquid that fulfilled the following conditions: 1) He atoms must be at least 2 Å away from any surrounding hydrogen or carbon atoms. 2) He atoms must be at least 12 Å apart from each other (which is the cut-off distance for interatomic forces). 3) He atoms must be at least 4 Å below the Gibbs dividing surface. This resulted in roughly between 10 and 20 He atoms in each liquid slab, and the atoms were given a kinetic energy corresponding to a 298 K Boltzmann distribution. After a period of a few ps during which E_{config} stabilised and equilibration was reached again, we monitored the position of all He atoms. Whenever a He atom passed through an imaginary plane parallel to and 20 Å above (or below as we have two surfaces) the liquid interfaces (where there is no longer any interaction between the surface and the He atom), its velocity was recorded and the atom not considered any further (i.e. it was ignored even if it re-entered the detection region due to the PBCs). This procedure was continued until around 75% of He atoms had evaporated, after typically ~70 ps, in order to avoid too many He atoms in the vacuum. We thus accumulated the velocities of ~10,000 He atoms, and these velocities were binned in 20 m s^{-1} wide intervals.

TABLE I. Parameters of the AMBER force field and UFF taken from Ref. 18 and 19.

bond	r_0 / Å	k_r / kJ mol^{-1}	
C–C	1.526	2594.1	
C–H	1.090	2845.1	
bend	θ_0 / °	k_θ / kJ mol^{-1}	
C–C–C	109.5	334.72	
C–C–H	109.5	418.4	
H–C–H	109.5	292.9	
torsion	A / kJ mol^{-1}	δ / °	m
X–C–C–X	2.93	0.0	3.0
atom	ϵ_{ii} / kJ mol^{-1}	σ_{ii} / Å	
C	0.1144	3.816	

H	0.0164	2.974
He	0.056	2.104

3. Results and Discussion

Using the configurational energy, E_{config}, as the indicator, relaxation of the pure dodecane slabs occurs after around 150 ps. We calculated the density of these pure dodecane slabs to be 713.3 g L^{-1} as compared to an experimental value of 746.0 g L^{-1}. Fig. 1 shows snapshots of a relaxed dodecane slab from above and from the side. Our procedure of extending the *z*-dimension of the initial liquid volume creates two liquid-vacuum interfaces. We did not during any of our simulations detect any dodecane molecules evaporating into the vacuum at our temperature of 298 K.[24] The density distributions along the *z*-dimension of 20,000 configurations recorded every 100 fs were averaged, and also averaged over the two opposite interfaces. The *z*-density distribution of the resulting interface was fitted to an equation of the form

$$\rho = \frac{1}{2}\,\rho_{\text{bulk}}\left[1 + \tanh\left\{\frac{2(z - z_0)}{d}\right\}\right]$$

Eqn. 8

where ρ and ρ_{bulk} are the densities along z and in the bulk, while z and z_0 are the positions perpendicular to the surface and the Gibbs dividing surface (z_0 is set to zero in Fig. 1c); d is the width of the interface which we calculate to be 8 Å for pure dodecane at 298 K. This is less than the value of 12 Å found by Sazhin and co-workers, however, their lowest temperature simulations were performed at 400 K.[25] The MD simulations reported here are at 298 K, and it has been shown that the thickness of the interface increases with increasing temperature. Less quantitatively, the roughness of the surface can be judged from Fig. 1, and thermal fluctuations are clearly visible.

Inserting He atoms into the liquid and binning the velocities of ~10,000 evaporating He atoms in 20 m s^{-1} intervals (as described in the Methods section) delivers a velocity distribution as shown in Fig. 2. These distributions can be directly compared to a distribution of thermal gas-phase He atoms at 298 K, but for the purpose of comparison have been fitted in this work to a distribution described by equation 9,

$$P(v)\mathrm{d}v = k\,v^3\,\exp\left[-\left(\frac{v - v_0}{\alpha}\right)^2\right]\mathrm{d}v$$

Eqn. 9

where k, v_0, and α are variables.[26] These fits consistently yielded distributions of evaporated He atoms which are fractionally faster than a thermal 298 K distribution, with an average translational energy of $(1.05 \pm 0.03) \times 2RT$.

The obtained average translation energies are a convenient measure to compare our data to the experimental work by Nathanson and co-workers, who find an average kinetic energy of

He atoms evaporating from 295 K liquid dodecane of $1.14 \times 2RT$,[8] albeit these data are for He atoms evaporating from a cylindrical jet. To allow for a better comparison, we have weighed our data by $\sin(\theta)^{-1}$ where θ is the polar angle of the evaporating He atoms with respect to the surface normal. This simulates a kinetic energy distribution if the He atoms in our calculations were evaporating from a cylindrical jet, leading to a slightly higher average kinetic energy of $(1.08 \pm 0.03) \times 2RT$. The agreement is not quantitative, and our deviation from a thermal distribution much smaller than in the experimental work; however, the standard deviation of our simulations allows us to conclude that the average kinetic energy is at least equal to or slightly larger than a thermal Maxwell-Boltzmann distribution.
In order to trace the origin of this slight deviation from a thermal Maxwell-Boltzmann velocity distribution, we calculated the contribution of the velocity component along the surface normal to the overall velocity (i.e. v_z/v) for each evaporating He atom, and averaged this ratio for all trajectories within a given velocity window, see Table 2.

Table 2: Average contribution of the velocity component perpendicular to the surface to the overall velocity (v_z/v) for four different velocity ranges.

He velocity range	v_z/v **(%)**
$v_{He} \leq 1000$ m s^{-1}	71 ± 21
1000 m s^{-1} $< v_{He} \leq 2000$ m s^{-1}	72 ± 21
2000 m s^{-1} $< v_{He} \leq 3000$ m s^{-1}	75 ± 20
$v_{He} > 3000$ m s^{-1}	76 ± 18

While the overall effect is small, and the standard deviation of data rather large, there is a noticeable increase in the contribution which the perpendicular velocity component makes to the overall velocity when moving to faster He atoms. It is, of course, not surprising to find that the evaporating He atoms have a pronounced v_z component as it is in the nature of evaporation that the atoms move away from the interface. The large standard deviation is simply a reflection of the expected $\cos\theta$ angular distribution which has not been analysed in detail in this work but will be subject of a future publication. However, this initial analysis indicates that mechanistically different trajectories may be responsible for the non-Maxwellian He velocity distributions.
Simulations have the advantage that they allow us to visualise He atoms as they evaporate from the liquid; in order to shed more light on the dynamics of evaporation, we hence visually inspected around 2000 trajectories which were randomly chosen but covered the whole velocity range. In doing so, it became apparent that some trajectories of evaporation display the same characteristics, and we loosely grouped the He atoms into three sections based on their evaporation mechanisms, with their typical spatial and translational evolution depicted in Fig. 3:

1) a He atom may find itself at the bottom of an inverted '*cone*' or 'crater' within the liquid surface and a few Ångstroms below the Gibbs dividing surface; it is repelled by alkyl chains

surrounding it from all sides but the top, so that the He atom experiences only forces accelerating it sideways and/or upwards where it evaporates through the hole, with no alkyl chains in its way. This effect may be amplified if the crater collapses from the liquid side, pushing the He atom outward, and results in fast He atoms.
2) He atoms move through the interfacial region but are 'captured' one last time by the van der Waals forces of the liquid interface, i.e. undergo one or two last *bounce(s)* with the surface before evaporating. These He atoms are often on a trajectory back towards the bulk (from the interfacial region) before undergoing a final bounce, i.e. they have a velocity vector whose *z* component points towards the bulk, but the last collision or two turns them around to have a velocity vector pointing away from the surface.
3) These He atoms *hover* just below or above the interface, undergoing a number of collisions before finally 'desorbing' from the liquid; these may move tens of Ångstroms parallel to the interface before evaporating, similar to a mobile atom desorbing from a flat metal surface.

While the three trajectories in Fig. 3 are distinctly different, there is nonetheless a continuous transition from one mechanism to the other, and any visual assignment is qualitative. However, inspection of around 2000 trajectories allowed us to determine that around 9% of all trajectories evaporate from within the inverted cones (1), ~18% through the hovering mechanism (3), and the majority (~73%) through the bouncing mechanism (2). The bouncing and hovering mechanisms each lead to He kinetic energy distributions that are close to a thermal Maxwell-Boltzmann distribution at 298 K. In fact, the collisions with dodecane chains seem to cause the bouncing mechanism to have a kinetic energy distribution only slightly hotter than a 298 K distribution, and conversely the hovering He atoms evaporate (or desorb) with a kinetic energy that is slightly colder than a thermal 298 K distribution. While the mechanism involving evaporation from inverted cones contributes little to the overall distribution, it seems to be the one mainly responsible for the faster than thermal overall kinetic energy distribution. The above points are shown in Figure 4 depicting the de-convolution of the overall kinetic energy distribution into three different components. For this purpose, we have converted velocity into energy distributions applying the appropriate Jacobian, namely $P(v)\mathrm{d}v=P(E)\mathrm{d}E$.[27]
It now becomes apparent that the *cone* mechanism in which the He atoms 'escape' from deeper within the liquid is responsible for the super-Maxwellian kinetic energy distribution determined experimentally and theoretically. The two other mechanisms (*bouncing* and *hovering*) are characterised by collisions of the He atom with surface molecules as can be seen in Fig. 3, and these are shown to moderate the kinetic energy of the evaporating He atoms towards a thermal Maxwell-Boltzmann distribution. The hovering mechanism is characterised by multiple collisional events with the surface, while the bouncing mechanism undergoes at least one collision with the surface, hence in both mechanisms do the He atoms undergo one or multiple final collisions with the surface, moderating their energy towards a thermal Maxwell-Boltzmann distribution.
In order to show these contributions more quantitatively, we plotted the evaporation probabilities $\beta(E) = P(E)/\,P_{\mathrm{MB}}(E)$ for each mechanism as a function of He kinetic energy,

see Fig. 5.[15] The kinetic energy distribution for each mechanism was normalised prior to division by a Maxwell-Boltzmann distribution, i.e. we show the deviation from a Maxwell-Boltzmann distribution for each component individually rather than its relative contribution. This shows clearly that the cone mechanism alone would result in a kinetic energy distribution far removed from a Maxwell-Boltzmann distribution; however, since the bounce mechanism contributes 73% to the overall distribution, the impact of the cone mechanism (9%) is small and barely surpasses the bounce mechanism if their relative contributions were considered even at the highest He kinetic energies.

4. Conclusions

We have simulated the evaporation of He atoms from liquid dodecane into vacuum using molecular dynamics methods. It has been found that the He atoms' velocity distribution is shifted to fractionally faster velocities as compared to a Maxwell-Boltzmann velocity distribution of He atoms at the temperature of the liquid surface. This result has qualitatively also been obtained in the experimental studies by Nathanson and co-workers,[8] but the effect is more pronounced in the liquid jet experiments than in the simulations. We have also established that faster He atoms have a slight preference to evaporate along the surface normal, i.e. they have a narrower angular distribution. Closer inspection of the trajectories of evaporating atoms reveals that most of the He atoms undergo multiple collisions on their way through the interface, moderating their kinetic energy towards a thermal Maxwell-Boltzmann distribution, but a small proportion of initially thermal He atoms emerges from the bottom of inverted cones or craters in the liquid surface; these atoms are repelled by the surrounding alkyl chains, and since the opening in the liquid surface of these craters is the only way to escape for these He atoms, they are ejected from these cones; the repulsive forces all sum up to direct the He atoms away from the liquid with a kinetic energy higher than thermal, resulting in this component being the main cause for the slightly shifted overall kinetic energy distribution.

ACKNOWLDGEMENTS

We thank the Dalton Cumbrian Facility program in part funded by the Nuclear Decommissioning Authority (NDA) for computational time, and Gilbert Nathanson, Fiona McLachlan and Richard Henchman for fruitful discussions; MW thanks the Computational Collaboration Project 5 (CCP5) for a bursary.

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Figure 1: a) Top-view and b) side-view of a relaxed dodecane slab; carbon atoms in red, hydrogen atoms in white. c) *z*-density profile of the vacuum-dodecane interface with the Gibbs dividing surface at zero, averaged over 100 ps. b) and c) are not on the same scale.

Fig. 2: Velocity distribution of He atoms evaporating from liquid dodecane. Open circles are the raw data from the MD simulations; blue line is a fit of these data to egn. 9 yielding an average translational energy of $(1.05 \pm 0.03) \times 2RT$. Red line is a Maxwell-Boltzmann velocity distribution of thermal He atoms at 298 K.

Fig. 3: Sample trajectories of the three different mechanisms of He evaporation as defined in the main text. The scale of each respective axis is the same throughout, left axis refers to the distance below (–ve) and above (+ve) the Gibbs dividing interface and data are in black, right axis is velocity and data are in red.

Fig. 4: De-convolution of the overall He kinetic energy distribution into contributions from the *bouncing* (red line), *skimming* (blue line), and *cone* (green line) mechanism according to ~2000 trajectories from the molecular dynamics simulations of He atoms evaporating from liquid dodecane. Dashed vertical lines are the maxima of the three curves.

Fig. 5: Relative evaporation probabilities for the three (normalised) contributions to the overall He kinetic energy distribution. Dotted horizontal line at $\beta(E) = 1$ is what one would expect for a perfect Maxwell-Boltzmann distribution.