Ab initio study of the atomic motion in liquid metal surfaces: comparison with Lennard-Jones systems

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Abstract
It is established that liquid metals exhibit surface layering at the liquid–vapour interface, while dielectric simple systems, like those interacting through Lennard-Jones potentials, show a monotonic decay from the liquid density to that of the vapour. First principles molecular dynamics simulations of the free liquid surface of several liquid metals (Li, Na, K, Rb, Cs, Mg, Ba, Al, Tl and Si), and the Na_3K_7 alloy near their triple points have been performed in order to study the atomic motion at the interface, mainly at the outer layer. Comparison with the results of classical molecular dynamics simulations of a Lennard-Jones system shows interesting differences and similarities. The probability distribution function of the time of residence in a layer shows a peak at very short times and a long-lasting tail. The mean residence time in a layer increases when approaching the interfacial region, slightly in the Lennard-Jones system but strongly in the metallic systems. The motion within the layers, parallel to the interface, can be described as diffusion enhanced (strongly in the case of the outermost layer) with respect to the bulk, for both types of systems, despite its reduced dimensionality in metals.

1. Introduction

Surface layering at metallic liquid free surfaces was suggested in the early 1980s by Monte Carlo simulations of alkali metal liquid surfaces [1]. Subsequently, more elaborate Monte Carlo techniques (see [2] and references therein), experimental measurements [3–10] and recent *ab initio* molecular dynamics (MD) simulations [11–16] have established that the ionic density profile of liquid metals across the interface shows oscillations that decay into the bulk liquid after, on average, three to four layers. The use of *ab initio* MD simulations in these studies is important for two reasons. First, being *ab initio*, the valence electrons and the ions are treated on the same footing, with the ions reacting consistently to the large spatial variations undergone by the electronic density when moving from the liquid to the vapour. Second, being MD simulations, a study of the motion of the atoms can be carried out directly and changes across the interface can be analysed. This type of study has not yet been undertaken, as far as we know, basically because most of the simulations of liquid metallic surfaces have been carried

out using the Monte Carlo method which gives no information about the dynamic properties of the system studied. The main aim of this paper is to fill this gap, reporting a study of the atomic motion in the free liquid surfaces of Li, Na, K, Rb, Cs, Mg, Ba, Al, Tl, Si and the Na_3K_7 alloy, using slabs with 2000 atoms. These results will, moreover, complement our previous study of the ionic and electronic structure of free liquid metal surfaces [16].

Layering also appears for metals at the solid–liquid interface [17] and for liquids in contact with a hard wall [18, 19] or in confined geometries [20]. Moreover, for ultrathin films of large molecules in contact with a Si wall [21] and for confined dusty plasma liquids [20] it has been possible to follow the molecular motion experimentally, whereas in the solid–liquid interface *ab initio* MD simulations allowed study of the atomic diffusion at the interface [17]. In all cases reduced diffusion with respect to the bulk was found.

These oscillating profiles are in contrast with those of the liquid–vapour interfaces of one-component dielectrics, like water or Lennard-Jones (LJ) systems, or those of liquid–liquid interfaces of immiscible mixtures, which show monotonic profiles with no layering. Taking the archetypal example of the one-component LJ system, we have found in the literature a large number of computer simulation studies of the coexisting densities, the interfacial width and the surface tension, as a function of the temperature, the particular LJ model used (truncated, truncated and shifted, full potential) and the lateral area simulated (see, for instance, [22] and references therein). However, to our knowledge, an analysis of the atomic motion in the interface has not yet been performed. Surprisingly, the situation is somewhat different for more complex systems, like water, or mixtures, where some (scarce) studies of atomic diffusion in the interfacial region have indeed been performed [23–26]. In the case of mixtures, some anisotropy in diffusion was detected, either due to an increase in the diffusion coefficient parallel to the interface, D_T, with respect to the bulk value [23, 24], or to a decrease of the diffusion coefficient normal to the interface, D_N, [25]. Following a thorough analysis of the effect of the inhomogeneity of the interface on the value (and even the definition) of D_N, molecular dynamics simulations of the liquid–vapour interface of water [26] revealed an increase in D_T (3.5-fold) and also in D_N (2-fold), which was attributed to a reduction in the number of hydrogen bonds in the interface. Moreover, it was argued that the same qualitative behaviour would occur for other simple liquids [26].

Although surface layering is common to the free surface of liquid metals and the systems mentioned above, there are also important differences. Even though the atoms in the outer layer of the interface rarely leave the liquid surface (especially at temperatures near their triple points), they are not geometrically confined. Moreover, in confined liquids, or liquids on a wall or at the interface with their solid phase, a strong interaction between the substrate and the first layers of the liquid has an important influence on the structure and dynamics of the liquid, leading to strong oscillations in the profile and to reduced diffusion. It is also worth analysing whether the free metallic surface, in particular the outer layer, behaves like a quasi two-dimensional system. There are some liquid alloys (Ga with small amounts of Tl, Pb or Bi) where the minority component, which has a high melting temperature and segregates to the surface, displays this kind of behaviour (see, for example, [27–29]). For one-component metals or other type of alloys, a possible measure of the two-dimensional character of the outer layer could be some distinctive feature of the density distribution function (DDF) of the time of residence of the atoms in that layer, for instance its mean value.

2. Simulation details

Because of the periodic boundary conditions used in most simulation methods, a slab geometry is usually adopted in studies of the liquid–vapour interface, with two free surfaces perpendicular

to one of the axes, taken here as the z-axis. These two surfaces should be well separated to minimize interaction between them. For the metallic systems we have performed *ab initio* MD simulations, whereas for the LJ system standard classical MDs have been used.

Ab initio simulations based on the Kohn–Sham formulation of the density functional theory (DFT) [30] pose huge computational demands, and the only metallic liquid surfaces studied so far, Si [11] and Na [12], used small samples (96 and 160 particles, respectively) where the two surfaces are rather close (16 and 20 Å, respectively). Orbital free *ab initio* molecular dynamics (OFAIMD) simulations reduce these computational demands somewhat by returning to the original Hohenberg–Kohn formulation of DFT [31], and adopting an explicit but approximate density functional for the electron kinetic energy so that the whole energy is a functional of the electron density. OFAIMD simulations of liquid metal surfaces have recently been performed [13–16] for the alkli metals Mg, Ba, Al, Tl, Si and Na_3K_7 using 2000 particles and for Li_4Na_6 using 3000 particles, which led to simulation boxes big enough to reliably represent a macroscopic interface. Details about the formalism and the electron–ion interactions can be found elsewhere [32, 33]. Even though the OFAIMD method has been applied successfully to bulk metals and alloys, it might be argued that this is not a sufficient validation of the method, as surfaces are different from bulk systems. However, it must be stressed that the OFAIMD studies of Na and Si produced results very similar to those obtained by the (in principle) more accurate Kohn–Sham *ab initio* simulations: the wavelength of the oscillations in the profiles, which is recovered exactly, the number of nearest neighbours of a Si particle across the interface, and the surface tension of liquid Na, are all well reproduced by the OFAIMD approach. Further confidence in the ability of the method to tackle metallic surfaces can be obtained from studies for finite systems, where the surface plays an essential role. For instance, a long-standing and previously unexplained anomalous variation of the melting temperatures of Na clusters with size [34] has been reproduced and rationalized for the first time in terms of the surface geometry and stability [35] using the same OFAIMD method as in this paper. Even more confidence in the capabilities of the method, concerning specifically semi-infinite surfaces, can be gained from preliminary results [36] obtained for the temperature dependent surface relaxation of Al(110) and Mg(10$\bar{1}$0), which reproduce qualitatively both experimental data and previous Kohn–Sham calculations.

The LJ system has been simulated at a reduced temperature $T^* = k_B T/\epsilon = 0.73$, which is near its triple point, in order to compare with the metallic systems in a similar thermodynamic state. We have made simulations with 1960 particles, similar to the metals, and also with 15 680 particles in order to reassess the results for the smaller system. The lateral side for the small system is 11.75σ, which is already large enough to suppress the unrealistic oscillatory behaviour of the interfacial properties due to periodic boundary conditions [37]. For the large system the lateral side is doubled (23.5σ), so the expected effects on the interfacial properties are only those of the enhanced capillary waves which should produce a wider interface than in the small system.

For all systems, the number of *NVE* equilibrium configurations used for averaging ranged between 20 000 and 30 000.

3. Layers definition

Figure 1 shows the ionic density profile obtained for liquid Si and the partial and total ionic density profiles for the liquid alloy Na_3K_7, while that of the LJ system is depicted in figure 2. The layers where the ionic motion was studied, which for metals were located between consecutive minima in the total ionic density profile, are also indicated. The outermost layer (numbered 1) comprises the region from the last minimum to the inflection point of the
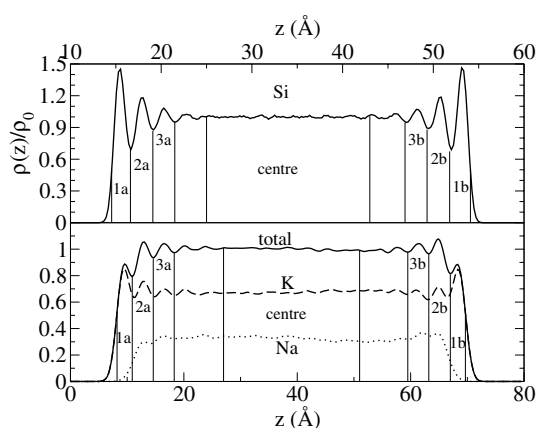
Figure 1. Ionic density profiles normal to the free liquid surfaces of Si and Na_3K_7. The different regions where the atomic motion has been studied are also shown.
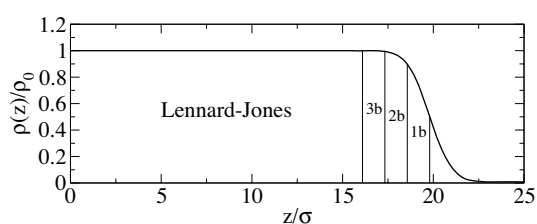

Figure 2. Ionic density profile normal to the liquid–vapour interface of the LJ system at $T^* = 0.73$, and the 'layers' defined for this interface. Only half the slab is shown.
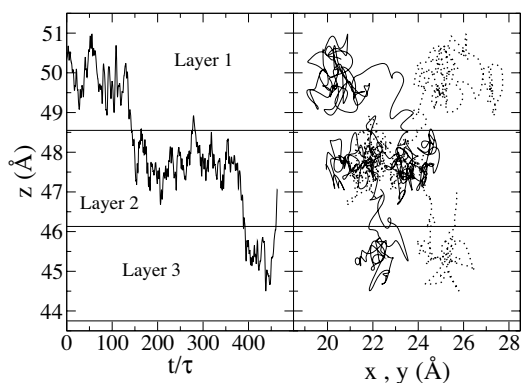

Figure 3. Time evolution of the z coordinate of an Al atom and its projected trajectory onto the xz (full line) and the yz (dotted line) planes.

decaying profile. For layers 1, 2 and 3 the results of the two layers on opposite sides of the slab were averaged. Further structural details of the interfaces of these systems have been given elsewhere [16], but we note here that the relative amplitudes of the outermost oscillation for the alkalis and alkaline earths are rather similar (maxima from 1.00 to 1.13, minima from 0.80 to 0.88), while they increase significantly for the systems of valence 3 and 4 (maxima 1.29, 1.47 and 1.56, minima 0.73, 0.69 and 0.54 for Al, Si and Tl, respectively).

The width of the different layers is very small, of the order of one atomic diameter. Therefore it is not appropriate to talk about diffusion along the direction normal to the interface within a layer, as there is no room for a particle within the layer to reach that type of motion. Figure 3 shows the time evolution of the z coordinate of one particular Al atom and an oscillatory-type motion within the layers can be seen followed by jumps into adjacent layers. The trajectory of the particle, projected onto the xz and yz planes, is also shown in the figure. To provide a meaningful comparison among the results for different systems, with diverse masses

and potentials, and consequently different characteristic times, a reference time, τ, has been defined for each system which is to be used as a time unit (see table 1). Specifically, τ has been taken as the first value of t for which the mean square displacement (MSD) in the bulk liquid has an inflection point, which is an indication of the atomic motion changing from free-particle to diffusive-like behaviour.

The ionic density profile for the large LJ system is shown in figure 2. For this type of system, the definition of 'layers' in order to analyse atomic motion is basically arbitrary. We have chosen to define them in a similar way as we have done for metals in order to make the comparison as fair as possible. First we have fitted the simulation results to an error function profile,

$$\rho(z) = \tfrac{1}{2}(\rho_\ell + \rho_v) + \tfrac{1}{2}(\rho_\ell - \rho_v)\text{erf}(\sqrt{\pi}(z_0 - z)/w)$$

(where ρ_ℓ and ρ_v are the coexisting densities of the liquid and the vapour, z_0 is the position of the interface, which coincides with the inflection point of the profile, and w is its width), which appears to be more adequate than the usual hyperbolic tangent one [38]. The widths for the small and large LJ systems are $w = 2.25\sigma$ and $w = 2.47\sigma$, respectively, the latter being larger, as expected from the increased number of capillary waves. In the following we will present the results obtained for the large system, which, apart from this interfacial width, are practically coincident with those for the small system. Layer number 1 is then defined as a slice of width $w/2$ from the inflection point towards the liquid. Further slices of width $w/2$ towards the liquid are then taken as layers 2 and 3. Note that, defined this way, the layers of the LJ system are also very thin (1.235σ), so we are in a similar situation as in metals, where we consider that diffusion is only possible within the layers parallel to the interface. The reference time τ for the LJ system is finally defined in the same way as for metals, and is also shown in table 1.

4. Results and discussion

In order to analyse the diffusive motion within the layers, the MSD along the x and y directions has been calculated for those particles that remain inside the layer for a long enough time (t_m), a criterion somewhat different from, although in the same spirit as, others used in previous works [25, 26]. The selection of t_m is somewhat delicate, as t_m must be large enough for diffusive motion to have already set in, but the number of particles that remain in a layer for at least t_m decreases as t_m increases, leading to poorer statistics. A good compromise was found to be $t_m = t_{20}$, defined so that the probability of residence in the layer for times larger than t_{20} is 20%. All the data shown below were obtained with this criterion, but checks showed that other reasonable choices for t_m led to statistically equivalent results. In order to compute t_{20}, and also to characterize the motion along the z-direction, the residence time of particles in each of the layers was studied.

4.1. Motion perpendicular to the interface

For all the systems considered, including the metals and the LJ system, the DDF of the residence time, $p(t)$, has been computed for the three outer layers (the case of Ba is shown in figure 4), and some common features can be identified. The maximum of $p(t)$ occurs at very small t-values, ($\approx \tau$), suggesting that most of the particles attempting to enter the layer are bounced back. Also, the DDF exhibits a long time tail, which gives rise to mean residence times (MRT), t_{av}, which increase when moving from the bulk liquid towards the outer layers (see table 1). In the LJ system this increase is rather small, amounting to approximately a 10%. For the metals, however, the MRT at the outermost layer is strongly enhanced, with increases between 75%

Table 1. Reference time, τ, mean residence time, t_{av}, 20% time (see text), t_{20}, ratio between D_T and the diffusion coefficient in the centre of the slab, D_{centre}, and Einstein frequencies for the systems considered and the different regions. The units of τ for the LJ system are standard reduced units, with picoseconds for all the other systems.

| System	τ	t_{av}/τ			t_{20}/τ			D_T/D_{centre}			$\Omega_z(\Omega_T)\tau$		
		Layer 1	Layer 2	Layer 3	Layer 1	Layer 2	Layer 3	Layer 1	Layer 2	Layer 3	Layer 1	Layer 2	Centre
LJ	0.167	11.1	10.6	10.5	18.7	17.7	17.2	1.94	1.13	0.96	—(—)	—(—)	—
Li	0.038	24.2	14.2	13.2	32.4	19.7	17.4	2.01	1.19	1.09	1.27(1.18)	1.58(1.51)	1.56
Na	0.105	17.6	11.0	10.1	26.3	16.6	14.6	2.16	1.18	1.12	1.37(1.29)	1.65(1.59)	1.60
K	0.170	19.5	11.6	10.8	26.8	16.8	15.0	2.19	1.21	1.08	1.35(1.28)	1.64(1.57)	1.59
Rb	0.284	19.5	11.3	10.6	27.7	16.9	15.6	2.10	1.22	1.08	1.36(1.29)	1.67(1.59)	1.61
Cs	0.352	20.3	12.0	10.6	32.2	17.0	15.3	1.81	1.13	1.07	1.41(1.35)	1.73(1.65)	1.67
Mg	0.056	22.5	12.0	11.1	33.7	17.7	15.2	2.27	1.29	1.09	1.33(1.33)	1.65(1.58)	1.61
Ba	0.158	24.6	13.5	12.8	25.1	16.5	14.5	2.02	1.22	1.08	1.30(1.28)	1.63(1.56)	1.55
Al	0.045	37.3	17.6	14.4	68.0	25.6	19.3	2.04	1.40	1.33	1.32(1.46)	1.66(1.62)	1.65
Tl	0.187	64.7	26.1	18.7	108.2	39.4	27.0	1.24	1.00	1.00	1.32(1.46)	1.65(1.60)	1.62
Si	0.058	21.4	9.5	7.8	37.4	16.3	13.3	1.24	1.00	1.00	1.68(1.87)	2.05(1.94)	1.97
Na@Na$_3$K$_7$	0.126	18.7		10.5	17.4		14.7	1.28		1.05	1.61(1.57)		1.61
K@Na$_3$K$_7$	0.176	18.9	10.2	9.8	29.4	15.2	14.4	2.24	1.25	1.06	1.39(1.28)	1.71(1.64)	1.67
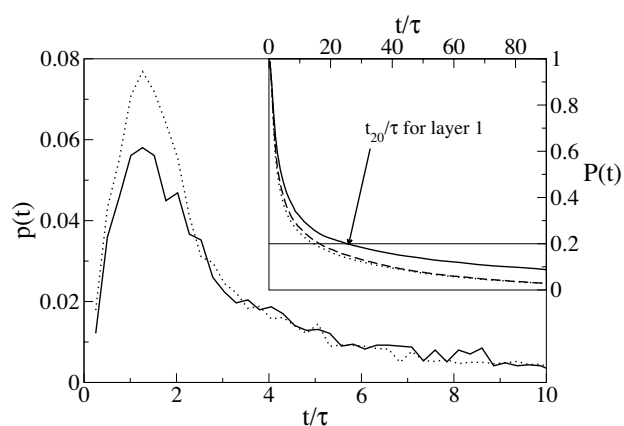
Figure 4. Distribution function of the residence time, $p(t)$, in layer 1 (full line) and layer 3 (dotted line) for liquid Ba. The inset shows the integrated probability distribution function, $P(t)$, together with the 20% level used to define t_{20}. The dashed line denotes layer 2.
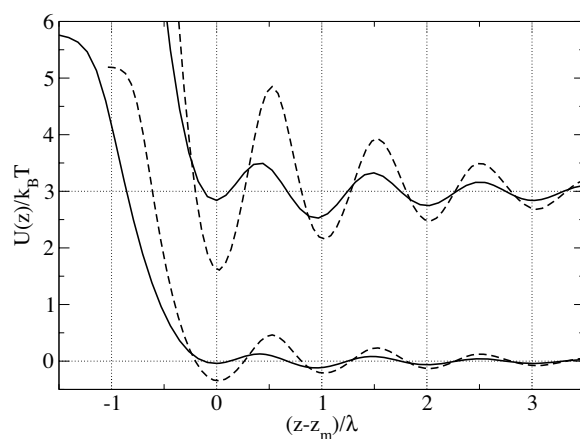

Figure 5. Energy barrier in terms of the thermal energy for Rb (full line) and Al (dashed line). The curves have been displaced (by z_m) and scaled (by λ) so that the positions of the extrema coincide for both systems. In these units the maxima of the density profiles occur at integer values. The upper curves are the same as the lower ones but multiplied by four and displaced upwards by three units.

(for Na) and 246% (for Tl), while the values taken at layer 2 show a more modest increase of around 10%. This large discrepancy between the behaviour of the LJ system and that of metals precludes any simple geometrical interpretation of the results and underlines that the change of interactions at the surface of liquid metals does have an important influence on some dynamic properties of the surface. Moreover, these results indicate that the outermost layer in metals behaves more bi-dimensionally than the inner ones. It is interesting to note that the MRT is around 20τ for the alkalis and alkaline-earths, whereas it increases in Al ($\approx 40\tau$) and Tl ($\approx 60\tau$), but not in Si.

In order to rationalize these differences among metals, we consider how the atoms move from one layer to another. The minima in the density profiles suggest the existence of an interlayer potential barrier, which would be higher the lower the minimum of the density profile. Therefore this barrier would increase significantly from the alkalis and alkaline earths to the polyvalent systems. We have estimated this barrier by integrating the profile of the z component of the force acting on the ions, and typical results are shown in figure 5, which includes data for Rb and Al and buttresses the expectations about the positions and heights of the interlayer energy barriers. It is also worth noting that the height of the barrier to be overcome by an atom in order to leave the surface is roughly one order of magnitude larger than the interlayer barrier height.
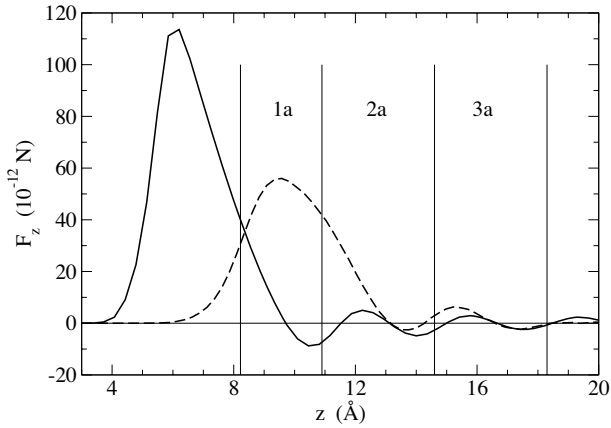
Figure 6. Profile of the z component of the force acting on K (full line) and Na (dashed line) atoms near the free surface of the liquid Na_3K_7 alloy. The vertical lines separate the different regions (see figure 1).

The probability of overcoming the interlayer barrier is related both to its height and to the frequency with which the atoms attempt to cross. This frequency has been estimated as proportional to the Einstein frequency along the z direction, Ω_z, which is shown in table 1 together with the corresponding frequency in the direction parallel to the interface, Ω_T, for completeness. These have been obtained from a short time (up to $t = \tau$) expansion of the corresponding MSD [39]. We find, in terms of τ, a rather universal value for all the systems except for Si, whose more open structure leads to higher Einstein frequencies. Therefore, the increase in the MRT of Al and Tl is related to the increased barrier height, whereas in Si the increased barrier height is counterbalanced by an increased Einstein frequency, leading to MRT similar to those of alkalis and alkaline earths.

The absence of well defined layers in the LJ profile suggests that the motion perpendicular to the interface is much easier than in metals, as no barriers are present, and therefore the position of our arbitrarily defined 'layers' has very little influence on the MRT.

Similar trends are also obtained for the liquid Na_3K_7 alloy, although surface segregation leads to an outer layer of almost pure K so that Na-related quantities are really irrelevant. Indeed the outermost Na layer comprises regions 1 and 2, and therefore the numbers shown in table 1 for Na in the alloy span columns 1 and 2 together. The profiles of the z component of the forces on the Na and K atoms are presented in figure 6, and underpin the previous statements, showing that Na atoms are subjected to an important repulsion when trying to move inside regions 1.

The integral $P(t) = \int_t^\infty p(u)\,du$ gives the probability that, having entered the layer, a particle remains there longer than t, and is used to obtain t_{20} (see the inset of figure 4). Values for t_{20} shown in table 1 correlate rather well with the MRT.

4.2. Motion parallel to the interface

The t_{20} times have been used to analyse the atomic motion within the layers. The MSD have been evaluated up to $0.8 \times t_{20}$, in order to allow an adequate averaging over the time origins. Figure 7 depicts the MSD for layers 1 and 2 and for the slab centre in liquid K. There is a clear increase in the slope as the interface is approached. This is common to all the systems, including the LJ one, and is quantified in table 1 which shows the ratio between the diffusion coefficient parallel to the interface, D_T, in the different layers and the bulk diffusion coefficient in the slab centre (where diffusion is isotropic).

We attribute this $\approx 100\%$ increase in the diffusion at the outermost layer to the reduced coordination of the atoms in the interface. In all the pure metals, except Si, the number of
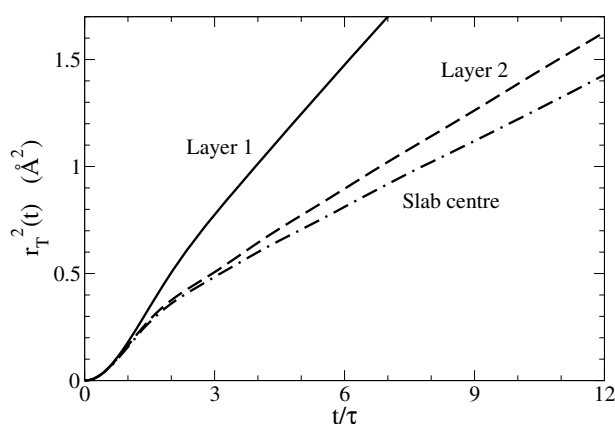
Figure 7. Mean square displacements for layers 1 and 2 and the slab centre for liquid K.

nearest neighbours is ≈ 12 at the centre of the slab and reduces to ≈ 8 at the outer layer. In the LJ system the coordination number again decreases from ≈ 12 to ≈ 9. For Si the coordination number is ≈ 6 at the centre and ≈ 4.5 at the outer layer. This smaller decrease is reflected in a smaller enhancement of the diffusion coefficient at the interface of only 24%. A similar explanation also holds for the Na_3K_7 alloy. The total number of neighbours around a K (Na) atom is roughly constant at ≈ 12.5 (10.0) up to regions 1, where it sharply decreases. Consequently, D_T for K increases rapidly in the outermost layer, whereas the value for Na in its outermost layer (regions 1 and 2) does not change significantly because very few Na atoms in regions 1 are affected by this decrease of coordination.

Other possible scenarios that could explain the large transverse diffusivity, like detachment from the surface followed by large transverse displacement and later reattachment at a different point on the surface, can be ruled out by the large magnitude of the interfacial barrier.

The case of Tl deserves special attention because the number of neighbours decreases from 12 to 8 but D_T increases by only 24% in the outermost layer. We attribute this modest increase in D_T in this strongly layered system to a large influence of the second layer on the atoms of the outermost one, an effect similar to that exerted by a wall on a liquid which leads to strong layering and reduced diffusion.

5. Conclusions

In summary, we have analysed through *ab initio* simulations the atomic motion in the free liquid surfaces of several metals and compared it with that of a LJ system in a similar thermodynamic state. Although the layered structure is similar to other systems such as liquids on a solid or in confined geometries, the dynamic behaviour within the layers is much more similar to the liquid–vapour interface of dielectrics, like the LJ system or water, showing an enhanced diffusion in the parallel direction at the interface, which is attributed to the reduced coordination of an atom which favours transverse movement. In the perpendicular direction, the layers are too thin to regard the motion as atomic diffusion, and instead the MRT associated with each layer has been determined. The dynamic behaviour of metallic systems along this direction is very different from that of LJ systems. The value of the MRT for metals is clearly larger at the outermost layer, contrary to the case of the LJ system, and increases significantly for polyvalent metals with closed structures. Finally, the reference time τ is found to be an excellent time unit, since it reveals universal values in several dynamic properties of different systems.

Acknowledgments

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