Nonequilibrium study of the intrinsic free-energy profile across a liquid-vapour interface

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We calculate an atomistically detailed free-energy profile across a heterogeneous system using a nonequilibrium approach. The path-integral formulation of Crooks fluctuation theorem is used in conjunction with the intrinsic sampling method (ISM) to calculate the free-energy profile for the liquid-vapour interface of the Lennard-Jones fluid. Free-energy barriers are found corresponding to the atomic layering in the liquid phase as well as a barrier associated with the presence of an adsorbed layer as revealed by the intrinsic density profile. Our findings are in agreement with profiles calculated using Widom’s potential distribution theorem applied to both the average and the intrinsic profiles as well as literature values for the excess chemical potential.

I. INTRODUCTION

The study of molecular transport across a fluid interface is of great importance in interfacial science. For instance, the transfer of ions or neutral components between two phases is a fundamental problem in biology and chemistry [1]. The interface introduces an activation barrier to the molecular transfer. The statistical mechanical description of this process was established by Kirkwood [2] using the free-energy profile or potential of mean force (PMF). This is a key property because it quantifies the driving force for molecular transport in the direction normal to the interface.

The direct calculation of the PMF by molecular simulation is often difficult due to inefficient sampling of the states of the system, in particular high free-energy domains characteristic of the interfacial region. Several methods have been developed to determine the PMF along an interfacial system (see, e.g. Darvas *et al.* [1, 3] and references therein). Examples range from constrained molecular dynamics [4] and umbrella biased simulations [5] to thermodynamic

integration [6, 7] and perturbation methods [8–10]. These have been applied to a variety of species across various fluid interfaces.

The aforementioned approaches employed to evaluate the PMF are *equilibrium* methods and have limitations both from a practical and theoretical perspective [11–14]. An alternative approach that has gained attention in recent years is based on the work of Jarzynski [15] and Crooks [16] which allows one to compute equilibrium free-energy differences from *nonequilibrium* thermodynamic path integrals. Taking the example of the transport of a molecule across an interface, a nonequilibrium approach is used to steer the molecule along the direction normal to the interface (cf. Fig. (1)) by applying an external driving force [17–20].

In the majority of previous calculations of the PMF across an interface, the free-energy profile is defined relative to the planar thermodynamic surface, e.g., the Gibbs dividing surface, that represents the average position of the interface throughout the course of the simulation. However, fluid interfaces are inherently rough and exhibit structure at the molecular level but appear smooth on average due to thermal capillary-wave fluctuations [21–23]. A variety of methods have been developed to represent the interface from a given molecular configuration taking this roughness into account [24–30]. In particular, the intrinsic sampling method (ISM) [31] is a self-consistent procedure that identifies

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a set of surface molecules which is used to define a mathematical surface expressed as a Fourier series. Unlike other methods, ISM has the added benefit of being physically consistent with capillary-wave theory [32, 33].

The intrinsic solvation free-energy profile of penetrants across a liquid-liquid interface has been computed in recent work using constrained molecular dynamics [34], coupled with a detailed analysis of the intrinsic surface [1, 3].

In our current paper, we take the vapour-liquid interface of the Lennard-Jones fluid as a prototypical example of a system with a free-energy barrier and compute the intrinsic free-energy profile using nonequilibrium molecular dynamics coupled with ISM to determine the intrinsic interface for each system configuration. This particular system is chosen as it is one of the most widely studied interfacial systems with a free-energy profile that can be expressed analytically using Widom's potential distribution theorem [35, 36].

In the next section, we outline the theoretical background including Widom's potential distribution theorem, Crooks fluctuation theorem, and capillary wave theory of a liquid vapour interface. Details of the simulation procedure are provided in section III. In section IV, the results are presented and discussed. The conclusions are given in section V.

II. THEORETICAL BACKGROUND

A. Equilibrium free-energy profiles

Equilibrium methods to compute the free-energy profile rely on the principle that at equilibrium the chemical potential is independent of position. The uniformity of the chemical potential is the main descriptor of the interfacial density profile. This relation has been explored in the past, e.g., by Leng *et al.* [37] and more notably by Widom [35, 36] through the application of the potential distribution theorem to a nonhomogeneous system.

For a system of N spherical particles in a volume V at a temperature T , Widom's expres-

sion for the chemical potential at a given point in the system can be expressed as

$$\mu = k_B T \ln \left(\frac{\rho(\mathbf{r})}{\langle e^{-\beta \Phi_1(\mathbf{r})} \rangle_{N-1}} \right) + 3k_B T \ln(\Lambda) \quad (1)$$

where $\rho(\mathbf{r}) = N \langle \delta(\mathbf{r}_1 - \mathbf{r}) \rangle$ is the density distribution at position $\mathbf{r}$, $\Lambda(\beta)$ is the thermal de Broglie wavelength, $\beta = 1/(k_B T)$ and $\Phi_1(\mathbf{r})$ is the potential energy of interaction of particle 1 with all of the others. As pointed out by Widom [35], both terms in the fraction in Eq. (1) are functions of position but their ratio is not. The invariance of the chemical potential provides a means to relate the average Boltzmann factor at given point to the corresponding density distribution

$$A(\mathbf{r}_1) = A(\mathbf{r}_0) - k_B T \ln \left(\frac{\rho(\mathbf{r}_1)}{\rho(\mathbf{r}_0)} \right) \quad (2)$$

where $A(\mathbf{r})$ is defined by the Boltzmann average

$$A(\mathbf{r}) = -k_B T \ln \langle e^{-\beta \Phi_1(\mathbf{r})} \rangle_{N-1} \quad (3)$$

Eq. (2) is an operational definition of the potential of mean force across the system as introduced by Kirkwood [2].

B. Nonequilibrium path-ensemble averages

The recent development of a set of statistical mechanical theorems [15, 16, 38–40] has opened the possibility of extracting equilibrium properties from nonequilibrium measurements where the system is driven dynamically over a finite period of time between two different states. The importance of these theorems stems from the fact that they are among the few exact relations for systems that are driven away from equilibrium [40]. In particular, the relations derived by Jarzynski [15] and by Crooks [16] relate the distribution of thermodynamic work done along a set of nonequilibrium paths connecting two equilibrium systems, to the difference in free energy between the two equilibrium states.

Consider a system in contact with a heat bath at constant temperature whose state $\mathbf{\Gamma}$ can be changed externally through a controllable parameter λ . Let W be the amount of work necessary to transform the system from an initial state at $t = 0$ described by the Hamiltonian $H(\mathbf{\Gamma}, \lambda_0)$ to a final state $H(\mathbf{\Gamma}, \lambda_\tau)$ at $t = \tau$. The reverse path, starting from $H(\mathbf{\Gamma}, \lambda_\tau)$, has a corresponding work $-W$. The Crooks fluctuation theorem (CFT) relates the work done to transform the system to the free energy difference between the final and initial states

$$\frac{P_f(W)}{P_r(-W)} = e^{\beta(W - \Delta A_\tau)} \quad (4)$$

where $P_f(W)$ and $P_r(-W)$ are the probabilities of expending a given amount of work W in the forward and reverse trajectories respectively, and ΔA_τ is the Helmholtz free-energy difference between the final and initial states. In the limit where the transformation between states is performed reversibly, $W = \Delta A_\tau$ in agreement with second law of thermodynamics. Crooks [41] further demonstrated that Eq. (4) may be seen as a special case of a single theorem

$$\langle F e^{-\beta W_{d,\tau}} \rangle_f = \langle \hat{F} \rangle_r \quad (5)$$

where the term on the right hand side is the path ensemble average of some functional F of the trajectories taken by the system through phase space. The subscript f indicates an average over a forward process where a system is perturbed from an initial equilibrium state to a final one over a set of paths. Each path is weighted by the corresponding dissipative work $W_{d,\tau}$, defined as the difference between the total work done on the system and the work along a reversible path. The right hand side of Eq. (5) corresponds to the reverse (subscript r) perturbation with $\hat{F}$ being the time reversal of F .

By choosing suitable forward and reverse path functions for a system of N particles, it can be shown that Eq. (5) gives (to within an additive constant) a relation between the unperturbed free-energy profile along a given direction (taken here as the z direction) and the

average over a set of nonequilibrium trajectories

$$e^{-\beta A(\xi)} = e^{\beta \Psi(\xi, \lambda_\tau)} \langle \delta(z_{N,\tau} - \xi) e^{-\beta W_\tau} \rangle_f \quad (6)$$

where $z_{N,\tau}$ is the position of particle N at time τ , and W_τ is the work performed to pull the particle during that period of time. For our purposes, Ψ is taken to be a time dependent harmonic potential acting on the N th particle in the z direction defined as

$$\Psi(\mathbf{r}_N, \lambda(t)) = \frac{\kappa_{spr}}{2} (z_N - \lambda(t))^2 \quad (7)$$

where κ_{spr} is the spring constant.

Given a set of nonequilibrium trajectories with the spring parameter changing in time at a constant rate $\lambda_t = \lambda_0 + vt$, let z_t be the value of probe atom position at time t for each trajectory. From the set of nonequilibrium trajectories, an ensemble of values $\{z_t\}$ and $\{W_t\}$ is obtained from which we can compute the corresponding distribution at each time t . At each time, the distributions will most probably be sampled adequately only around the equilibrium position λ_t . The complete free-energy profile can be obtained using the adaptation of the Ferrenberg and Swendsen weighted histogram method [42] as described by Hummer and Szabo [18]

$$A(\xi) = -k_B T \ln \left(\frac{\sum_t \frac{\langle \delta(z_t - \xi) e^{-\beta W_t} \rangle_f}{\langle e^{-\beta W_t} \rangle_f}}{\sum_t \frac{e^{-\beta \Psi(\xi, \lambda_t)}}{\langle e^{-\beta W_t} \rangle_f}} \right) \quad (8)$$

where Jarzynski's identity is used as an estimator for the free-energy difference ΔA_t between the initial and the state of the system at time t .

C. Capillary-wave theory

Capillary-wave theory (CWT) incorporates the surface roughness of an interface with planar area $\mathcal{A}_0$ by defining an *intrinsic* surface [32] $z = \xi(\mathbf{R}, q_u)$, representing the instantaneous

microscopic boundary between the liquid and the vapour phases for each transverse position $\mathbf{R} = (x, y)$ of the system. In the CWT one assumes that the intrinsic surface can be represented as a Fourier series

$$\xi(\mathbf{R}, q_u) = \hat{\xi}_0 + \sum_{0 < |\mathbf{q}| < q_u} \hat{\xi}_{\mathbf{q}} e^{i \mathbf{q} \cdot \mathbf{R}} \quad (9)$$

where $\langle \hat{\xi}_0 \rangle$ represents the mean planar position of the interface. The wavevector cutoff q_u is chosen to correspond to a wavelength commensurate with the atomic radius σ . Using this definition, the corresponding intrinsic density profile can be defined as

$$\tilde{\rho}(z, q_u) = \left\langle \frac{1}{\mathcal{A}_0} \sum_{i=1}^N \delta(z - z_i + \xi(\mathbf{R}_i, q_u)) \right\rangle \quad (10)$$

where $(\mathbf{R}_i, z_i)$ represents the set of atomic transverse coordinates of a given configuration. As the system evolves over time, so does $\xi(\mathbf{R}, q_u)$. The motivation of our current work is to use the intrinsic surface to analyse the work distributions of a set of nonequilibrium trajectories driving the probe particle from the liquid to the vapour phases. The intrinsic surface allows us to remove the averaging effect of the interface thermal fluctuations from the computed free energy profiles.

III. MODEL AND SIMULATION DETAILS

All simulations are conducted on a system of atoms interacting through a spherically truncated and shifted Lennard-Jones (LJ) 12-6 potential $\phi(r)$ with a cutoff radius of $r_{cut} = 2.5\sigma$

$$\phi(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] - \phi(r_{cut}) \quad (11)$$

where r is the distance between a pair of particles and the corresponding energy and length scales are defined by ϵ and σ , respectively. Unless otherwise indicated, reduced units are used throughout this work.

The vapour-liquid interface is modelled using a system of $N = 6000$ particles inside a simulation cell of dimensions $L_x = L_y = 12.0$ and $L_z = 120.0$. The initial configuration is set up by placing the particles inside a central volume $L_x = L_y = 12.0$ and $L_z = 52.0$ giving a initial liquid phase density close to the value $\rho = 0.7861$ at $T = 0.7$ reported by Trokhymchuk and Alejandre [43]. In order to avoid dependencies on system size, Trokhymchuk and Alejandre [43] recommended computer simulations using at least $N = 1000$ particles. Furthermore, the short dimension of the simulation box was chosen to be larger than $L_x \approx 10$ to avoid boundary condition effects that introduce spurious correlations in the interface fluctuations as described by Bresme *et al.* [44].

Two temperatures are considered, $T = 0.6$ and $T = 0.7$, in order to investigate the effect of temperature on the interface corrugations and their impact on the resulting free energy profiles.

The temperatures chosen are relatively low in order to emphasise the effects of a dense fluid with a sharp vapour-liquid interface. For the LJ potential various values of the triple point temperature have been reported: Mastny and de Pablo give a value of $T = 0.694$ [45]. It has also been shown, however, that there is strong dependence of the triple point value on the cutoff of the LJ potential used in calculations. Studies on the effect of the potential truncation on the solid-liquid phase coexistence lead one to conclude that a cutoff of $r_{cut} = 2.5$ lowers the triple point temperature as compared to that exhibited by the full potential [46]. As a representative value, the triple point of the (shifted force) LJ fluid with a cutoff of 2.5 is determined as $T = 0.560$ [47].

To ensure that the system is above its triple point temperature we compute the pair radial distribution functions for the dense phase at temperatures of both $T = 0.6$ and $T = 0.7$ (cf. Fig. (2)). It is apparent that there is no evidence of solid-phase structure at either temperature, ensuring that we are in the stable fluid region.

For each temperature, the system is equilib-

rated for 10^6 steps using a timestep $\Delta t = 0.001$. The temperature is controlled using a Nosé-Hoover [48, 49] thermostat with mass $m_\eta = 50.0$. The equations of motion are integrated using the LAMMPS software package [50].

Following the initial equilibration phase, each system is simulated for a further 10^6 steps from which 1000 independent liquid-vapour configurations are sampled at a frequency of 1000 time steps. Four replicas of each configuration are generated by reinitialising the velocities from a Boltzmann distribution at the corresponding temperature, resulting in a total of 4000 replicas of the same liquid-vapour system. Each replica is then integrated for 10^5 steps to allow it to relax from the initial state. This set of configurations constitutes the initial ensemble from which both equilibrium and nonequilibrium simulations are conducted respectively.

The equilibrium properties of each system are computed by running simulations in the canonical ensemble over the initial ensemble of trajectories. Each configuration is integrated for a further 10^5 steps over which the average properties are computed giving a total of 10^8 samples.

The simulation of each nonequilibrium trajectory is performed in two stages. The first stage sets up the initial conditions for the trajectory. Using the equilibrium average interface positions as a reference point, a judicious choice for the initial position of the probe atom is taken by tethering its z coordinate to $z_0 = 16.0$ using a spring constant $\kappa_{spr} = 500.0$ for 10^5 time steps. Starting from the initial position, the probe atom is pulled in the positive z direction using the harmonic guiding potential defined in Eq. (7). A system at the start of a nonequilibrium trajectory with the probe atom tethered to its initial position is illustrated in Fig. (1). The spring constant is chosen to be $\kappa_{spr} = 5.0$ and its equilibrium position changes over time at constant rate

$$\lambda(t) = \lambda(0) + v_{spr} t \quad (12)$$

where $\lambda(0) = z_0 = 16.0$ and $v_{spr} = 0.005$. Each trajectory was simulated for 4×10^6 time steps with the spring stopping at its final position $\lambda(\tau) = 36.0$ after travelling a distance

$\lambda(\tau) - \lambda(0) = 20.0$. Through each trajectory the probe atom will sample the different regions of interest in the system - liquid phase, interfacial region and gas phase. For a sufficiently high number of pulling trajectories, the free-energy profile across the different regions of interest can be evaluated using a histogram technique. Following the procedure outlined by Hummer and Szabo [18], the position of the probe atom z_t , the spring position $\lambda(t)$, the interface position $\xi(\mathbf{R}_t, q_u)$, where $\mathbf{R}_t = (x_t, y_t)$ are the coordinates of the probe atom at time t , and the accumulated work w_t are recorded for each trajectory $k = 1, \dots, K$ where $K = 4000$. Taking the time derivative of Eq. (7) to describe the rate of change of the system energy, the accumulated work at time t is given by

$$\begin{aligned} w_t &= \int_0^t dt' \frac{\partial H}{\partial t'} \\ &= \kappa_{spr} v_{spr} \left(\frac{v_{spr}^2 t^2}{2} - \int_0^t dt' (z_{t'} - \lambda(0)) \right) \end{aligned} \quad (13)$$

For each trajectory 1000 discrete time points t_i are sampled at a frequency of 4000 time steps. Let z_{ki} , $\lambda_i = \lambda(0) + v_{spr} t_i$, and $\xi_{ki} = \xi(\mathbf{R}_{ki}, q_u)$ be the positions of the atom, spring, and interface at time t_i for trajectory κ_{spr} , respectively. Similarly, let Ψ_{ki} , w_{ki} , and $\eta_{ki} = \exp(-\beta w_{ki})$ be the spring biasing energy, accumulated work, and corresponding Boltzmann factor at time t_i for the trajectory κ_{spr} , respectively. From the ensemble of positions and accumulated work at each time frame t_i , the free-energy profile is reconstructed using Eq. (8).

Figure 1: Snapshot of a liquid-vapour system at $T = 0.6$ at the start of a nonequilibrium trajectory. The fluid atoms (blue) constitute the liquid-vapour system and the probe atom (red) is tethered to its initial position. The arrow indicates the direction of the spring velocity.

IV. RESULTS AND DISCUSSION

The average density profiles for the two temperatures are shown in Fig. (3). From these, the average interface position on the right hand side is determined to be $z_i = 24.91$ for $T = 0.6$ and $z_i = 26.33$ for $T = 0.7$ respectively (cf. Table (I)). The resulting densities of the liquid and vapour phases at each temperature are collected in Table (I), and are found to be in very good agreement with the results reported by Trokhymchuk and Alejandre [43] ($\rho_l = 0.7852$, $\rho_v = 0.0067$) and by Adams and Henderson [51] ($\rho_l = 0.787$, $\rho_v = 0.006$).

The corresponding intrinsic density profiles are presented in Fig. (4). The removal of the effect of thermal fluctuations from the density profiles gives rise to the molecular structure at the interface as captured by the density peaks in the liquid phase, as well as an adsorption peak at $z \approx 1.0$ in agreement with the results reported by Chacon and co-workers [31, 52] and Bresme and co-workers [44, 53]. The bulk densities correspond to those given by the average profile. The delta peak at $z = 0.0$ reflects the contributions from the surface sites to the intrinsic profile, with a density $N_s/\mathcal{A}_0$, as defined by the intrinsic surface computation [31, 44]. Due to the discretization of distance to the interface in the histogram calculation, the density peak at the origin is not a true delta function but can be approximated by a Gaussian of the

form

$$\frac{N_s}{\mathcal{A}_0} \delta(z) \approx \frac{N_s}{\mathcal{A}_0 \sqrt{2\pi\omega^2}} e^{-z^2/2\omega^2} \quad (14)$$

where the magnitude of the standard deviation is given by half the bin width $\omega = 0.06$. This gives the value of the density at $z = 0$ as

$$\bar{\rho}(0) = \frac{N_s}{\mathcal{A}_0} \delta(0) = \frac{N_s}{\mathcal{A}_0 \sqrt{2\pi\omega^2}} \quad (15)$$

Figure 2: Pair radial distribution functions of the liquid phase at $T = 0.6$ and $\rho = 0.837$ (green curve) and at $T = 0.7$ and $\rho = 0.787$ (red curve).

Table I: Structure of the average liquid-vapour interfaces. ρ_l is the liquid phase density, ρ_v is the vapour phase density, $z_{i,left}$ and $z_{i,right}$ are the negative and positive average positions of the interface in the z direction and h_i is the average interface width.

T	ρ_l	ρ_v	$z_{i,left}$	$z_{i,right}$	h_i
0.6	0.837	0.002	-24.74	24.91	0.64
0.7	0.787	0.007	-26.05	26.33	0.81

Figure 3: Average density profiles at $T = 0.6$ (green curve) and at $T = 0.7$ (red curve) as a function of distance z .

Figure 4: Intrinsic density profiles at $T = 0.6$ (green curve) and at $T = 0.7$ (red curve).

The application of Crooks fluctuation theorem to the calculation of the free-energy profiles at $T = 0.6$ and $T = 0.7$ is shown in Fig. (5) and Fig. (6) respectively. The red and green symbols depict the nonequilibrium results obtained when using the average and instantaneous interface positions respectively, defined by Eq. (9). The continuous black curve on each

profile illustrates the application of Widom's potential distribution theorem, Eq. (2), to the average and intrinsic density profiles.

We observe at $T = 0.7$ that there is small but significant difference between the free-energy profiles. It can be seen that there is quantitative agreement between the free-energy profiles obtained via the application of CFT and Widom's potential distribution theorem for both representations of the interface.

When the instantaneous interface position is used in the calculation of the atom position, we observe the appearance of free-energy barriers in the vicinity of the interface associated with the layered structure of the fluid near the surface in the liquid phase. Furthermore, in the gas phase at $z \approx 1.2$, a local barrier reflecting the presence of the adsorbed layer in the vapour phase can be observed in agreement with the results of Chacon and Tarazona [31].

Again, at $z = 0.0$, we observe the presence of a sharp minima corresponding to the presence of the surface atoms when computing the interface at the highest level of resolution. For each temperature, the value of this minima is directly dependent on our choice for the histogram bin width. More precisely,

$$A(0) \approx -k_B T \ln \left(\frac{N_s}{\rho_l \mathcal{A}_0 \sqrt{2\pi\omega^2}} \right). \quad (16)$$

Using the bulk density values in Table (I), the above expression gives $A(0) \approx -1.1$ at $T = 0.6$ and $A(0) \approx -1.3$ at $T = 0.7$ for our choice of surface density $N_s/\mathcal{A}_0 = 0.8$ respectively.

If the mean interface position is used instead, the structural detail in the free-energy profile is lost because the interfacial region has been smeared out. At $T = 0.7$, a small but significant difference between the nonequilibrium profiles and those obtained by application of Widom's potential distribution theorem can be observed (cf. Fig. (6)). A possible explanation is that due to the lower surface tension of the liquid at higher temperatures, the probe molecule may induce larger local interfacial deformations biasing the free-energy profile to higher values at distances smaller than the cutoff ($r_{cut} = 2.5$).

Figure 5: Free energy profile as function of the atomic position with respect to the interface at $T = 0.6$. The red and green symbols depict the nonequilibrium results obtained when using the average and instantaneous interface positions respectively. Solid black curves illustrate the application of Widom's potential distribution theorem to the average and intrinsic density profiles.

V. CONCLUSIONS

We have applied the path integral formulation of Crooks Fluctuation Theorem to the calculation of the free-energy profile across an heterogeneous system. In particular, the free-energy profile is calculated as a function of the position relative to the interface for a liquid-vapour system at different thermodynamic conditions.

It is recognised that the interface has a detailed structure at the microscopic scale. Thermal fluctuations of the interface induce a blurring of the thermodynamic properties, in particular the density and free-energy profiles. The intrinsic sampling method is used to take these fluctuations into account, enabling a precise calculation of the free-energy features in the interfacial region.

We have demonstrated that this approach is valid for a simple Lennard-Jones system where

Figure 6: Free energy profile as function of the atomic position with respect to the interface at $T = 0.7$. The red and green symbols depict the nonequilibrium results obtained when using the average and instantaneous interface positions respectively. Solid black curves illustrate the application of Widom's potential distribution theorem to the average and intrinsic density profiles.

the free-energy profile can be calculated exactly. The resulting free-energy profiles exhibit microscopic details not apparent when using a mean-field approach where the interfacial fluctuations induce a spatial averaging of the thermodynamic properties across the interface. In particular, we find free-energy barriers associated with the layered structure of the fluid near the surface in the liquid phase, as well as a barrier associated with the adsorbed layer in the vapour phase. The positions of these barriers are consistent with the peaks in the intrinsic density profiles. Furthermore, our results are in quantitative agreement with the free-energy profiles calculated using Widom's potential distribution theorem applied to both the intrinsic density profile and its mean-field counterpart.

This gives a more complex picture for the transport of a molecule from one phase to another as it will have to cross a series of energy barriers which may ultimately define the rate

of interphase mass transfer. The impact on the molecular dynamical properties can be significant in cases such as ionic liquids, where these barriers are expected to be large, and also in the case of structured molecules where orientational transitions are induced as the molecule crosses the interface. The non equilibrium approach can potentially be useful in studying the energy of adsorption of more complex structures (e.g. amphiphilic molecules) in liquid-vapour water systems [54, 55].

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