**Methodology LEMTA**

LEMTA have gathered a unique group of competences with the best experts in the field that are not available anywhere else. Concerning the simulations, the main tools is *Molecular dynamics and Monte Carlo simulations.*

Chart, diagram

Description automatically generated

**Fig. 1.** Examples of interactions: a) a model representation of the water molecule based on the three sites model (SPC and SPCE/); b) an example of interaction of a water molecule with the uncharged solid substrate; c) example of the Lenard-Jones interactional potentials.

For numerical modelling of the solid/liquid interaction close to a nanostructured interface, the main tool that we plan to use is atomistic modelling with molecular dynamics (MD). Molecular dynamics methods are the best suited approaches for the description of heat and mass transfer across interfaces at nanoscales. As a powerful tool to elucidate heat transport processes in multiphase systems it will bring new and valuable contributions to the before mentioned problems in connection with the description of heat and mass transfer. In principle, any type of gas, liquid, solid states, and inter-phase phenomena can be solved without the knowledge of macroscopic "thermo-physical properties" such as thermal conductivity, viscosity, latent heat, saturation temperature and surface tension. The numerical data such as temperature, energy, atom motion, structural factor, etc. evaluated with MD technique will provide a basis for the further micro- and mesoscopic simulations. In addition, consideration of “micro-geometry” of the interface is a promising way to improve ultimately macroscopic behaviour of efficient systems and devices.

Chart

Description automatically generated with low confidence

**Fig. 2.** a) molecular dynamics snapshot of a water droplet on silicon substrate: cylindrical droplet morphology was chosen to minimise impact of the line tension; b) density map of the liquid inside droplet; c) dependence of the wetting angle of the considered droplet and a spherical one as a function of Lenard-Jones interactional parameter21

Principle: MD uses classical Newton’s equations of motion to describe the system evolution with a large number of degrees of freedom. Because of its specificity one needs to initialize simulations by setting an initial configuration for the positions of atoms and molecules. Then construction of geometry and morphological nanoscale features of contacting interfaces can be performed. It is therefore possible to simulate different kinds of structuration of the solid surface. Evolution of the system based on the atoms movements with respect to the interatomic forces (see **Fig. 1**) and external fields in presence gives an inside regarding numerous processes arising at the nanoscale31. More specifically, implementation of the wave-packet formalism gives us the information regarding to phonon scattering at the interfaces32 which is crucial to understand energy transfer. These data will relate to the parameters that define interaction between solid and liquid in the same way as PI did for wetting angle (see **Fig. 2**).

*Equilibrium and non-equilibrium Molecular Dynamics:*

As it was mentioned previously, one can evaluate heat and mass transfer in the heterogeneous solid-fluid composite media featuring the interface with the use of MD approaches. As an example, non-equilibrium MD (NEMD) and equilibrium MD (EMD) for thermal conductivity evaluation can be mentioned33. Both approaches can be used to study diffusion and viscosity effects of liquid layer adjusted to solid substrate, heat transfer coefficients from solid to fluid, boundary thermal resistance of interface between solid and fluid, etc. These parameters are critical to apply conservation of mass, momentum, and energy in classical macroscopic models of heat and mass transfers, and fluid mechanics. MD was successfully applied for the study of thermal and mass transport across the solid/fluid interface34–36. However, almost all approaches presented in the literature were limited to the case of smooth interfaces. The main goal of the project will be focused on the investigation of the influence of heterogeneity of solid surface on molecular and thermal transport across the interface. Additionally, in the project the influence of the nano-impurities in liquid (nanoparticles) contacting with solid substrate on the thermal and mass transport coefficients will be considered.

Below we present a list of MD methods that will be used during the project implementation.

Both equilibrium (EMD) and non-equilibrium (NEMD) are based on the time-reversible equations of motion. The NEMD shows a consistent macroscopic basis for the irreversible macroscopic second law of thermodynamics37,38. The main idea for using NEMD is to apply spatial distribution of the controlled variables like temperature (heating and cooling distinct regions as seen in Fig. 2), constraint, pressure, or heat flux37. On the other hand, when using EMD, we consider fluctuations of the system around equilibrium. As a well-known example, for calculation of thermal conductivity in the system one can use the following equation based on Green-Kubo formalism:

where is the thermal conductivity, V is the volume of considered system, T is the temperature, is the heat flux in “*ith*” direction. The main advantage of this approach is the possibility to obtain directly the anisotropy of thermal transport in the studied system at equilibrium. This has a significant importance for the investigations of hybrid systems with liquids, hence temperature gradients imposed in NEMD can modify the liquids properties. However, there are still debates regarding implementation of this approach for the study of heterogeneous system. Therefore, one of the important challenges of the project will be to verify the applicability of the equilibrium-based methods to hybrid systems. If no we will propose the necessary modifications.

*Tool 2 - Raman spectroscopy*

The typical sketch-view of the Raman setup is presented in **Fig. 3 a**. In this case the laser beam is focused on the sample surface, and the reflected (or transmitted for transparent samples) light is collected by the same optical system. Then reflected light is filtered by the notch or edge filter to cut the excitation laser wavelength, and in a such way scattered light is further analysed by spectrometer.

|  |  |
| --- | --- |
| Diagram  Description automatically generated with medium confidence | **Fig. 3.** a) A schematic sketch-view of the Raman set-up; b) dependence of the optical phonon peak of silicon on temperature (extracted from46); c) Stokes/Anti-stokes peaks for silicon |

Raman scattering is the inelastic scattering of a light by a matter. It takes place when phonons transfer (for Stokes process) a portion of energy to the molecular vibrations. Specifically, the peaks in the Raman spectra correspond to the high frequency phonons for solids. Therefore, the positions of the peaks are sensitive to the strains in the material. Because of thermoelastic property, it can be used for the temperature measurements in the light beam focusing area. As an example, the dependence of the silicon peak of the optical phonons position on the temperature is presented in **Fig. 3 b**.

Another possibility of the temperature sensing is based on the measurements of the Stokes/Anti-stokes ratiothat is also sensitive to the temperature (see Fig. 8 c):

where and are the intensities of the Strokes and Anti-stokes peaks, is the constant that depends on the set-up configuration, and are the wavelengths of the scattered light due to the Stokes and Anti-stokes processes, is the frequency corresponded to the Raman peak.

Thus, Raman spectroscopy allows us to investigate the temperature response of thin systems (with characteristic sizes ~1 µm), and simultaneously the laser light can be used as a heating source. This allows us to study the temperature rise in the sample as a function of the source power, and one can evaluate thermal conductivity of the samples based on the thermal problem resolution. Specifically, PI of the project proposed the method of thermal transport anisotropy study based on the laser beam shape modifications47,48.

*Tool 3 - Scanning thermal microscopy*

Principle: Scanning thermal microscopy (SThM) is based on the Atomic Force Microscope (AFM) where a nanoscale tip interacts directly with a surface. Regular AFM experiments can give us the insightful information on the topography of the interfaces such as roughness or its periodicity or structuration at a nanoscale level. We will go further by using the SThM technique developed in the team. Briefly, in SThM we use a thermoresistive tip that heats up by Joule effect (when a small electrical current flow through the probe creating a nano-heat source as large as the tip (~100nm)). Raster scans along a surface of a sample give us the topographic information on the roughness or structuration of the interface and images of the heat transferred from the hot probe to the surface with a lateral resolution of ~100nm. The schematic representation of the basic principle of the SThM is shown in Fig. 4.

Diagram

Description automatically generated

**Fig. 4.** Schematic sketch-view of the SThM measurements setup

Major improvements have been done to the SThM developed in the team in order to carry out quantitative information from the measurements. First, the system has been integrated in a controlled environment chamber where the pressure can be lowered to high vacuum (~10-6mbar) in order to control humidity and/or to get rid of undesired convection losses.

Within the framework of this project we will use the introduced setup in an innovative manner by coupling the hot tip with a thin liquid layer in order to accurately study the energy transfer from the solid phase to the liquid as well as the interface effect. Moreover, such coupling has never been attempted before that makes our setup unique in this area.

*Tool 4 - Time Domain Thermoreflectance (TDTR)*

Principle: Time domain thermoreflectance by using the femtosecond laser is also a very powerful technique to study nanoscale energy transfers due to its unparalleled temporal resolution (less than 10-12sec that can be easily reach by using the optical sampling). For example, the picosecond ultrasonic can be used in more precise measurements of extremely thin thickness, and in studying of the acoustic wave propagation. It has also been successfully applied in the field of nanoscale heat transfer to measure thermal conductivity of solid and liquid samples as well as Kapitza interface resistance between various materials.

The basic principle of the pump-probe TDTR is simple: a brief laser pulse is used to generate the acoustic or heat waves through the absorption of the laser energy by a thin metallic transducer. Then a second delayed laser pulse is used to monitore the variation of the optical properties of this transducer. The delay between the two laser pulses is obtained by a mechanical delay line. The acoustic or the electro-optic modulator is also combined with a lock-in detection to improve the signal, to noise the ratio, and to detect tiny variations (ΔR/R ~10-5) of the transducer reflectivity.

An example of the typical femtosecond pump-probe TDTR and measured thermal/acoustical signal is given in the following figure.

Diagram

Description automatically generated

**Fig. 5.** Left: the classical femtosecond TDTR setup. Middle: the sample capped with a thin metallic transducer. Right: the typical thermoreflectance contained both heat transfer and acoustical wave propagation.

While this femtosecond pump-probe setup may be hardly built by novice, our team at LEMTA has a great experience in building such setup.