



Practical session 2

Calculation of a surface tensión (L/V) and a interfacial tensión (L/L) from molecular dynamics simulations:

- *n-hexane (ST)*
- *n-hexane/water (IFT)*

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Interfacial or surface tension (IFT or ST, γ) arises from unbalanced attractive forces between two different phases. This leads to an excess of free energy at interface (i.e., surface free energy). Formally, γ is the force per unit length that opposes the growth of the surface area. For a system at constant pressure (or volume), temperature and composition:

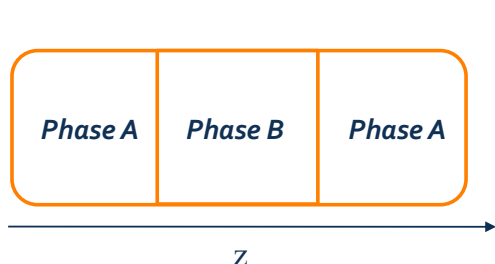
$$\gamma = \left(\frac{\partial G}{\partial \mathcal{A}} \right)_{N,P,T} = \left(\frac{\partial A}{\partial \mathcal{A}} \right)_{N,V,T}$$

*where G and A are the Gibbs and Helmholtz free energies, respectively, and \mathcal{A} is the surface area. The common units for IFT are **dynes/cm** or **mN/m**.*

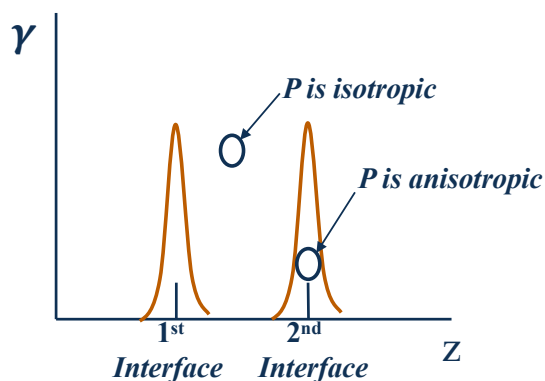
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γ can be calculated using the **Kirkwood-Buff method** (i.e., **pressure tensor method**), based on that this tensor is diagonal for a planar interface in an inhomogeneous fluid at hydrostatic equilibrium, being the independent components (i.e., normal P_n and tangential P_t ones) a function of only z :

$$\gamma = \int_{-\infty}^{\infty} dz [P_n(z) - P_t(z)] = \frac{L_z}{2} \left(P_{zz} - \frac{P_{xx} + P_{yy}}{2} \right) \quad (2 \text{ interfaces})$$



$$\langle \gamma \rangle = \frac{1}{2} \left(\langle P_{zz} \rangle - \frac{\langle P_{xx} \rangle + \langle P_{yy} \rangle}{2} \right) \langle L_z \rangle$$



$$P_{\alpha\beta} = \frac{1}{V} \left[\sum_{i=1}^N m_i v_{i\alpha} v_{i\beta} + \sum_{i=1}^{N-1} \sum_{j=i+1}^N F_{ij\alpha} r_{ij\beta} \right]$$

α, β → x, y or z
 $v_{i\alpha}$ → velocities
 $F_{ij\alpha}$ → forces between i and j
 $r_{ij\beta}$ → distances between i and j

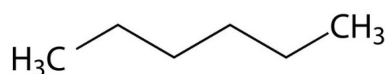
Calculation of N-hexane surface tension

Computational method:

- **Molecular Dynamics** (numerical integration of Newton equations)
- **TraPPE** force field (which fits exp. phase equilibrium data):

$$U_{\text{total}} = \sum_{i=1}^N \sum_{j>i}^N U_{ij}, \quad U_{ij} = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}} + K_{ij} (r_{ij} - r_{ij}^0) + K'_{ij} (\theta_{ij} - \theta_{ij}^0) + \dots$$

- **TraPPE-UA** (united-atom) representations for alkyl groups (i.e., hydrogen atoms are modelled implicitly along with the carbon atoms they are bonded to in a single pseudoatom type:



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- **LAMMPS** (Large-scale Atomic/Molecular Massively Parallel Simulator) is an **open-source** classical molecular dynamics code
- **Orthorhombic simulation cell**: $30 \text{ \AA} \times 30 \text{ \AA} \times 90 \text{ \AA}$ (1/3 hexane + 2/3 vacuum):



$$N_{\text{molec}} = \frac{L_x \cdot L_y \cdot L_z (\text{\AA}^3)}{3} \cdot 10^{-24} \cdot \rho_L (\text{g / cm}^3) \cdot \frac{1}{M (\text{g / mol})} \cdot 6.023 \times 10^{23}$$

($\rho_L(T, P)$)

- Firstly, there will be a minimization using a soft potential and later with TraPPE force field
- Canonical ensemble (**NVT**) ($T = 25^\circ \text{ C}$); Nose-Hoover thermostat

– *Inputs:*

run.in: read all simulation parameters (i.e., L_x , L_y , L_z , T , steps ...).

hexane.in: contains the structure of a single hexane molecule (read by *run.in*).

potential.ff: contains the force field parameters (read by *run.in*).

– *Outputs:*

lammps.out: shows the simulation parameters and the different calculated properties at several timesteps.

lammps.ave: gives the total energy and IFT at several timesteps.

lammps.xyz: gives the geometry of the system at different timesteps (can be open with AVOGADRO in QUBUNTU).

(*log.lammps*, *err.lammps*, *out.lammps*)

– *Execution:*

A) *Using QUBUNTU OS (LAMMPS_2017):*

- *open a terminal*
- *create directories /PS2/ST and /PS2/IFT*
- *cd to the folder /PS2/ST*
- *download the files from UAM (Moodle) or from cerqt2.qt.ub.es:*
e.g., *scp your_user@cerqt2.qt.ub.edu:/work/MEAS/PS2/ST/*.*
- *lammps < run.in > lammps.out & (execute in background)*

B) Using an external cluster, IQTCUB (LAMMPS_2015):

- *Connect to the cluster (ssh):*
ssh -l -X your_user cerqt2.qt.ub.edu (or ssh -l -Y)
- *Make several directories in your home:*
mkdir PS2 , mkdir ./PS2/ST , mkdir ./PS2/IFT
- *Copy input files and scripts from /work/MEAS/PS2/ST and /work/MEAS/PS2/IFT into your directories ST and IFT:*
cd PS2/ST
cp /work/MEAS/PS2/ST/ . (the same for IFT)*
- *Send your calculation with LAMMPS to a batch queue:*
qsub -N name lammeps_sub (put a name for the calculation)
qstat (show the status of your job)

Input: run.in

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#====Simulation Settings====#
units                real    # Define units in Å, fs, kcal/mol, K, atm
boundary p p p      # The simulation cell is periodic in all directions of the space
dimension            3      # The simulation cell is 3-Dimensional
atom_style full      # Define the system as a molecular set (atoms with bonds or no-bonds, etc)

#====Simulation Variables====#
variable Cutoff      equal    12      # Cutoff distance for intermolecular interactions (Å)
variable T            equal    298.15  # Temperature (K)
timestep 2           # Timestep (fs)
thermo 100           # Print thermodynamic output each 100 steps

#==== Box Parameters and Molecular PPTs ====#
variable X            equal    30.0    # x
variable Y            equal    30.0    # y
variable Z            equal    90.0    # z dimension length (Å)
variable Rho1         equal    0.65478  # Density of hexane at 298.15 K (g/cm3)
variable PM1          equal    86.1756  # Molar mass of hexane (g/mol)

#-----Load Molecules-----#
molecule mol1 hexane.in      # Load a molecule file

# Calculate the number of molecules to add in the sym box as a function of Rho, PM and
# XYZ cell parameters. This variable fills 1/3 of the simulation cell (1 var per molec) #
variable N1           equal    floor(${X}*${Y}*(${Z}/3)/1e24*6.023E23*${Rho1}/${PM1}) #

#==== Box Creation ====#
lattice custom 1. a1 $X 0. 0. a2 0. $Y 0. 0. a3 0. 0. $Z basis 0. 0. 0. #

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10011101C
10101011C
10101011C
101011101
10000001C
iqtc
Institut de Química Teòrica
i Computacional

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region sym block 0 1 0 1 0 1 units lattice #
create_box 4 sym bond/types 2 angle/types 2 dihedral/types 1 extra/bond/per/atom 10
               extra/angle/per/atom 10 extra/dihedral/per/atom 40 extra/special/per/atom 25
#===== Region Definition & Atom Creation=====#
region Liquid block 0 1 0 1 0 0.33 units lattice # cubic region
create_atoms 0 random ${N1} 298437 Liquid mol mol1 301709 # add moles to liquid region:seeds
#===== OUTPUT VARIABLES=====#
variable IFT equal (-((zhi-zlo)/2.0)*(((pxx+pyy)/2.0)-pzz))*0.0101325 # Calculate IFT (mN/m)
variable TotEng equal etotal # Calculate Etotal
fix averages all ave/time 1 10000 10000 v_TotEng v_IFT file lammps.ave # Write file lammps.ave
dump trj all xyz 10000 lammps.xyz # Write traj. each 10000 timesteps
thermo_style custom step temp pzz vol pe ke etotal v_IFT # What to print (you may add new keys)
#===== Minimization Process With Soft Potential at 10 K and rigid molecules=====#
include potential.ff # Load the whole FF
pair_style soft 3 # Change the LJ pair by Soft
pair_coeff * * 1 # Soft parameters
fix label1 all rigid/nvt molecule temp 10 10 200 # Time evolution scheme (10 K)
run 10000 # run during 10000 steps
unfix label1 # Erase time evolution scheme
#===== Simulation with appropriate Potential and non-rigid molecules=====#
include potential.ff # Load the whole FF
fix label1 all nvt temp $T $T 200 # Time evolution scheme (298.15 K)
run 100000 # run during 100000 steps
unfix label1 # Erase time evolution scheme

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Output: lammps.out

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.....
Step      Temp      Pzz  Volume  PotEng  KinEng  v_TotEng  v_IFT
10000    3.3335007  2330.9684  81000  271.10029  7.3232244  278.42352  324.10379
10100    271.87976 -941.59129  81000 -258.74581  597.28095  338.53514  18.771706
10200    305.21599  557.67716  81000 -261.20921  670.51589  409.30668  153.55887
10300    294.24464  967.44243  81000 -186.91727  646.41341  459.49613  9.1051444
10400    309.64623  1112.6867  81000 -206.50046  680.24848  473.74802  35.670532
10500    305.58060  -73.4973  81000 -226.99238  671.31689  444.32451 -62.052718
10600    294.51994 -713.2272  81000 -225.60224  647.01819  421.41595  64.068068
.....

```

Total wall time: 5 – 18 min depending on the node/processors (110000 steps)

Output: lammps.ave

Step	v_TotEng	v_IFT
10000	39.339	-1.04291
20000	362.216	7.53937
30000	92.6918	23.366
40000	-39.9584	11.2557
50000	-58.6288	18.6262
60000	-97.4793	12.9189

.....

(mN/m or dyn/cm) → v_IFT

(kcal/mol) → v_TotEng

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Experimental data (NIST web/JANAF/Springer) for water

T (° C)	ρ_L (g/cm ³)	ρ_V (g/cm ³)	P _v (torr)	γ (dyn/cm)
25	0.9971	2.3075×10^{-5}	23.78	71.98
40	0.9922	5.1242×10^{-5}	55.39	69.59
60	0.9832	1.3×10^{-4}	149.41	66.24

Experimental data (*) for *n*-hexane/water

T (° C)	γ (dyn/cm)
25	50.38
40	48.92
60	47.29

* (*J. Chem. Eng. Data* 46 (2001) 1086)

Additional slides

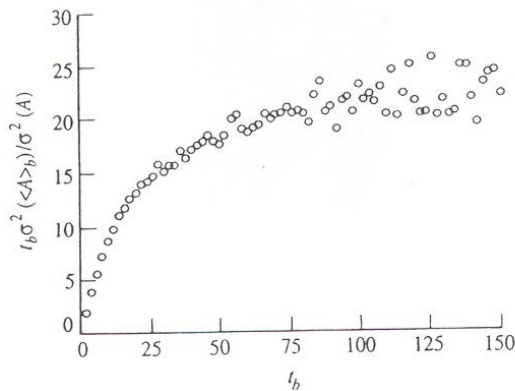
It can be estimated previously to the simulation

Is the variance of the block averages.
Inversely proportional to t_b

Statistical errors

The statistical inefficiency or relaxation time is calculated as:

$$s = \lim_{t_b \rightarrow \infty} \frac{t_b \sigma^2(\langle A_b \rangle)}{\sigma^2(A)}$$



With N configuration, just $M = N/s$ will be uncorrelated

The error in the averaged value when calculated from a finite simulation:

$$\sigma(\langle A \rangle) = \sigma(A) \sqrt{\frac{s}{N}}$$