Manual for LPC3D (Lattice_Porous_Carbon_3D.c)

Some information describing the lattice model for porous carbons is related here:
Merlet et al., *J. Chem. Phys.*, **142**, 094701 (2015)
and available at:
http://scitation.aip.org/content/aip/journal/jcp/142/9/10.1063/1.4913368
and
http://arxiv.org/abs/1412.7043

A description of the model with applied potentials is related here:
Belhboub et al., *Electrochim. Acta*, **327**, 135022 (2019)
and available at:
https://www.sciencedirect.com/science/article/pii/S0013468619318936
and
https://arxiv.org/abs/1910.02663

Contents

1 Introduction

This program is a lattice model to calculate quantities of adsorbed ions, diffusion coefficients and predict NMR spectra of ions adsorbed in porous carbon matrices.

- For diffusion coefficients calculations, data derived from molecular dynamics simulations is used as input to determine in-pore adsorption profiles, and data from experiments is used to obtain energy barriers governing transitions between lattice sites.
- For NMR spectra calculations, the model uses chemical shifts obtained from density functional theory calculations.

2 Types of simulation

In this model, only one carbon electrode is simulated and its structure is represented as a cubic tridimensional set of inter-connected discrete sites, separated by a lattice spacing.

In its current state, the program can deal with three main types of simulations:

- "planar": The system is a unique slit pore with parallel pore walls. This corresponds to the first model described in J. Chem. Phys., 142, 094701 (2015). In this type of simulation, one lattice site is equivalent to one position in a pore and the chemical shift is assigned depending on the z coordinate only.
- "porous": The system is a complex 3D geometry of obstacles and free sites. No results are published on this yet. In this type of simulation, one lattice site is either an obstacle or a position in a pore. At this point, the chemical shift is assigned depending on the smallest 'considered site' - 'non accessible site' distance. The position of the obstacles is obtained following atomic positions of a porous structure: according to a given probe size, all the sites on a 3D grid are defined as accessible or non accessible.
- "coarse": The system is a collection of slit pores with different pore widths and pore surfaces. This corresponds to the second model described in J. Chem. Phys., 142, 094701 (2015). In this type of simulation, one lattice site is equivalent to one pore and the chemical shift is assigned following the results of the "planar" model.

3 Compiling the program

The program is written in C and is not parallel. To compile it, you can use any C compiler, e.g. gcc:

gcc -o LPC3D.x Lattice_Porous_Carbon_3D_28-10-2019.c -lm

4 Running the program

After compilation, the program can be run using the following command line:

./LPC3D.x < input_file

5 Formats of input file

The beginning of the input file is the same for the three types of simulations:

- 1st line: numbers of lattice sites in x, y and z directions ($> Nx$, Ny, Nz)
- 2nd line: lattice parameter in Å ($> a$)
- 3nd line: dwell time in seconds ($> dwell$)
- 4th line: number of steps between measures ($> nsample$)

- 5th line: temperature in Kelvin ($> T$)
- 6th line: Larmor frequency of the studied nucleus under the magnetic field considered in MHz ($> larmorfreq$)
- 7th line: random seed for the steps involving random ($> seed$)
- 8th line: obstacles ($> test\_latt$)
  - 0: no obstacles, all sites are accessible
  - 1: lattice given from a previous run or built differently
  - 2: obstacles assigned randomly, some sites are unaccessible
  - 3: obstacles defined according to positions of carbon atoms
- 9th line:
  - no 9th line if $test\_latt = 0$
  - name of the obstacles' file if $test\_latt = 1$ ($> namelatt$)
  - coverage if $test\_latt = 2$ ($> coverage$)
  - name of the positions' file and minimum distance if $test\_latt = 3$ ($> namepos$, $Dmin$)
    positions' file = xyz file with coordinates in the same units as the lattice parameter
- 10th line: number of values for the Fourier transform ($> Nvalues$)
  Please use an even number of values.
- 11th line: pulse sequence ($> pseq$)
  - "single": single pulse
  - "echo": spin echo = 90^{o} - tau - 180^{o} - tau

  At this date, the echo pulse sequence has not been validated.
- 12th line: type of the simulation ($> simtype$)

After this line, the files differ depending on the type of simulation.

5.1 "Planar" type simulations

- 13th line: name of the file with the free energies ($> nameeng$)
  The first column should be in Å, the second column should be in kJ.mol^{-1}.
- 14th line: number of free energies values = number of lines in the *nameeng* file ($> Neng$)
- 15th line: do we use the values directly, do we build a pore or do we use Xing fit? ($> poreshift$)
  - "Xing": uses the model described in Xing et al., Carbon, 77, 1132 (2014)
  - "direct": uses the values from the file named in the following line assuming that the chemical shift given in $namefreq$ is the total chemical shift due to both pore walls
  - "indirect": uses the values from the file named in the following line assuming that the chemical shift given in $namefreq$ is the chemical shift due to one pore wall (so applying additivity rules to obtain the total chemical shift, see Forse et al., J. Phys. Chem. C, 118, 7508 (2014) for details about the additivity)
- 16th line: name of the file with the resonance frequencies if direct/indirect before ($> namefreq$)
  The first column should be in Å, the second column should be in ppm.
- 17th line: number of frequencies if direct/indirect before ($> Nfreq$)

Note, there are no 16th and 17th line if the poreshift option chosen is "Xing".

```
1 1 81
0.5
4.919e-5
10
298
300
2345
1
Network_walls_81.dat
5000
single
planar
free_ener_anions_0V.dat
250
indirect
nics_circumcoronene.dat
201
```

Input example for "planar" type simulations.

5.2 "Porous" type simulations

- 13th line: type of free energies assignment ($> test_feng$)
  It can be"1D" if we use a one dimensional profile or "3D" if we use a three dimensional matrix
- 14th line: name of the file with the free energies ($> nameeng$)
  The first column should be in Å, the second column should be in kJ.mol^{-1}.
- 15th line: number of free energies values ($> Neng$)
- 16th line: do we use the values directly or do we use Xing fit? ($> poreshift$)
  - "Xing": uses the model described in Xing et al., Carbon, 77, 1132 (2014)
  - "direct": uses the values from the file named in the following line assuming that the chemical shift given in $namefreq$ is the total chemical shift due to both pore walls
  - "indirect": uses the values from the file named in the following line assuming that the chemical shift given in $namefreq$ is the chemical shift due to one pore wall (so applying additivity rules to obtain the total chemical shift, see Forse et al., J. Phys. Chem. C, 118, 7508 (2014) for details about the additivity)
- 17th line: name of the file with the frequencies if direct before ($> namefreq$)
  The first column should be in Å, the second column should be in ppm.
- 18th line: number of frequencies if direct before ($> Nfreq$)

Note, there are no 17th and 18th line if the poreshift option chosen is "Xing".

```
1.0
1
298.0
300.0
2345
3
Carbon_QMD_1x.xyz 3.0
1000
single
porous
1D
free_ener_anions_0V.dat
250
direct
nics_circumcoronene.dat
201
```

Input example for "porous" type simulations.

5.3 "Coarse" type simulations

- 13th line: number of integrated densities values ($> Npores$)
  It is equal to the number of frequencies.

- following line: how to read the integrated densities (> *densread*)
  - distinguished to read anion, cation and solvent separately
  - undistinguished, to consider only one species
- following line: name of the file(s) with the integrated densities of anions and cations (if distinguished reading) or considered species (if undistinguished reading).
  The unit does not really matter as long as the ratios of densities are correct.
- (if distinguished reading) following line: solvent consideration "solvent_ON" or "solvent_OFF" (> *solvent_activ*)
- (if distinguished reading) following line: name of the file with the integrated density of solvent if solvent_ON
- (if distinguished reading) following line: type of molecule (= anion, cation or solvent) for which diffusion and NMR calculations will be performed (> *iontype*)
- following lines (3): names of the files with the frequencies and area of the corresponding molecules in $Å^2$ (> $namefreq1$, $area[1]$, $namefreq2$, $area[2]$, $namefreq3$, $area[3]$)
  In the $namefreqi$ files, the first column should be in Å and the second column should be in ppm.
  ATTENTION THEY SHOULD BE GIVEN IN THE ORDER OF INCREASING AREAS!
  For more details on the use of these areas, see Merlet et al., J. Chem. Phys., 142, 094701 (2015).
- Pore size distribution options:
  - following line: log normal distribution or discrete values for the pore size distribution (> *psdtype*)
    "lognormal" if the pore size distribution was fitted to a log normal function
    "discrete" if the pore size distribution is directly taken from the experimental data
  - (if *psdtype* = "lognormal") following line: mean and standard deviation for the log normal distribution of pore sizes (> *meanpsd*, *stdpsd*)
  - (if *psdtype* = "discrete") following line: psd reading = "mono" for one psd or "mixed" for two psds (> *psdread*)
  - (if *psdread* = "mono") following line: name of the file with the pore size distribution and number of lines (> *namepsd*, *nlinespsd*)
  - (if *psdread* = "mixed") following line: name of the first file with a pore size distribution and number of lines (> *namepsd*, *nlinespsd*)
  - (if *psdread* = "mixed") following line: name of the second file with a pore size distribution and number of lines (> *namepsdm*, *nlinespsdm*)
  - (if *psdread* = "mixed") following line: mixing ratio (> *mixratio*) which should give the percentage of pores of type 1 in the total system (corresponding to the first declared psd)
- Pore surface distribution options:
  - following line: log normal distribution or discrete values for the surface distribution (> $surftype$)
    "lognormal" if the surface distribution is a log normal function
    "discrete" if the surface distribution is a discrete function
  - (if $surftype$ = "lognormal") mean and standard deviation for the log normal distribution of surface sizes (> $meansurf$, $stdsurf$)
  - (if $surftype$ = "discrete") name of the file with the surface size distribution and number of lines (> $namesurf$, $nlinessurf$)
- Energy barriers options:
  - following line: calculation of the energy barriers (> *Enbar_mode*)
    0 for random gaussian distribution
    1 for energies calculated from fit of experimental data (see Forse el al. Nat. Ener. (2016) 2, 16216)
  - (if *Enbar_mode* = 0) following line: mean and standard deviation for the Gaussian distribution of barrier heights (> *meanEa*, *stdEa*)

  - (if $Enbar\_mode = 1$) following line: reference temperature at which the energy barriers are calculated ($> T\_ref$)

- following line: gradient of pore sizes? 0 if no, 1 if yes ($> gradient$)
  N.B.: SIMULATIONS OF LATTICES WITH GRADIENT PORE DISTRIBUTIONS MAY PRODUCE SOME INSTABILITIES!

- Ionic properties options:

  - (if distinguished reading) following line: volumes of the anion, cation, solvent molecules and cell voltage in this order ($> Vanion$, $Vcation$, $Vsolvent$, $volt$) if solvent is considered ("solvent_ON") otherwise reading only $Vanion$, $Vcation$ and $volt$
  - (if undistinguished reading) following line: volume of the considered particle ($> Vspec$), and cell voltage ($> volt$)
  - (if distinguished reading) following line: molecular mass of the anion, cation and solvent in this order ($> anionmass$, $cationmass$, $solventmass$).
    For solvent consideration: same as the reading of volumes.
  - (if undistinguished reading) following line: molecular mass of the particle ($> mspec$)

- following line: number of steps for the equilibration process ($> step$) and equilibrium threshold ($> thrsld$)

- following line: writing density files during equilibration = "wrtdns_on" to write files, "wrtdns_off" to not write files ($> wrtdns$); and number of steps between two density checks = number of steps if "wrtdns_on" (non-zero value) or 0 if "wrtdns_off" ($> nsmple$)

- following line: minimum in-pore density to be considered for calculations ($> rhotrshld$)
  N.B.: To compare results of different calculations, the same minimum in-pore density threshold should be considered as the chosen threshold directly impacts the considered PSD (i.e. the carbon structure).

- following line: distribution preferences of obstacles = "small" for putting obstacles on small pores, "large" for putting obstacles on large pores, "none" for putting obstacles randomly with no consideration of pore dimensions ($> Cover\_pref$)
  N.B.: THIS OPTION SHOULD BE SPECIFIED ONLY IF $test\_latt = 2$

- following line: particle size in lattice units = -1 or larger than lattice size → the particle is the full box, 0 → there is only bulk, between 0 and Nx → there is a particle and bulk around ($> particlesize$)

```
20 20 20
1.0
5e-06
1
300.0
300.0
12345
0
50000
single
coarse
3490
distinguished
Int_dens_pore_size_BF4_EMIBF4_1Vpos.dat
Int_dens_pore_size_EMI_EMIBF4_1Vpos.dat
solvent_OFF
cation
Avg_shift_pore_size_coronene_EMI_1Vpos.dat 36.200
Avg_shift_pore_size_circumcoronene_EMI_1Vpos.dat 98.100
Avg_shift_pore_size_dicircumcoronene_EMI_1Vpos.dat 191.100
discrete
mixed
PSD-STC-8-micro.dat  36
PSD-STC-8-meso.dat  53
0.25
lognormal
-0.10 0.25
1
298.0
0
48.000 99.314 1.0
87.000 111.092
10000 1e-06
wrtdns_on 10
1e-20
large
-1
```

Input example for “coarse” type simulations.