

Modelling Physical Adsorption on Finite Objects Using 3 Dimensional Non-Local Density Functional Theory 2: Effects of Physical Parameters and Higher-Order Effects

*J. P. Olivier, Senior Staff Scientist, retired
Micromeritics Instrument Corporation, Norcross GA USA*

Non-local density functional theory (NLDFT) has recently [1] been productively extended from its “classical” one-dimensional form to two dimensions, allowing the treatment of some finite objects, such as discs, and to incorporate some significant forms of surface heterogeneity. Since the NLDFT theory underlies most current methods for extracting the surface area and pore size distribution of industrially important materials from adsorption data, it seems appropriate to critically reevaluate it against experimental data.

While NLDFT captures some major phenomena, such as phase transitions in porous materials and the step-wise layer formation of isotherms on uniform surfaces such as highly graphitized carbon, it over-predicts the slope of the monolayer region; the locations of succeeding layers are also not in good agreement with data. To better understand this problem, it seemed advisable also to extend the dimensionality to three dimensions.

In an initial report [2], we described chiefly considerations of the model itself, such as the size and granularity of the 3-dimensional computational grid and its adjacent “free space”. An important code verification step was recovering the isotherm of an unstructured surface, produced from the classical 1-D theory, from the central region of a 3-D 5 nm square graphite nanochip using the same parameters, thus also suggesting a route to a “quasi-infinite” isotherm for an atomistic surface of infinite extent.

It has been frequently noted in the literature that NLDFT appears to overestimate the adsorbate-adsorbate attractive component of the chemical potential by approximately 15%: this quantity is normally calculated using the Lenard-Jones 6-12 formulation with the WCA approximation to avoid the singularity. Since the same energy parameter is derived from the saturation pressure states of the adsorptive, it is clear that any deviation must be a function correlated with distance from the surface. One possibility proposed [3] is the presence of a surface-dipole field leading to a repulsive potential between surface induced parallel dipoles. Other possibilities stem from the very high densities of the adsorbate molecules in the first few adsorbed layers, equivalent to megapascal pressures. Ustinov [4] has convincingly suggested the importance of three-body effects. In this work, we look more quantitatively at physical parameters of the model and their formulation, as well as the possibilities suggested above, with respect to deviations from the experimental data.

While the computational tasks remain challenging, technical advances in multi-core processors with large vectorization registers and the corresponding software to enable parallel processing have allowed us to start down the path toward modelling adsorption on three dimensional atomistic surfaces of arbitrary shape employing NLDFT, using the Tarazona prescriptions for the hard sphere Helmholtz free energy functional.

- 1) J. Jagiello, J. P. Olivier, *2D-NLDFT adsorption models for carbon slit-shaped pores with surface energetical heterogeneity and geometrical corrugation*, Carbon **55**, 70-80, 2013
- 2) J. P. Olivier, *Modelling Physical Adsorption on Finite Objects Using 3 Dimensional NLDFT. 1: Initial Studies, Presented at World Conference on Carbon 2018, Madrid, Spain.*
- 3) J. P. Olivier, J. Jagiello, *The contribution of surface field induced dipoles to fluid-fluid and fluid-solid adsorptive potentials as modelled by NLDFT*, Presented at: World Conference on carbon, Clemson, S..C., 2010.
- 4) E. Ustinov, *Effect of three-body interactions on Ar adsorption on graphitized carbon black.*, J. Chem. Phys., **132**, 194703 (2010)