



WHITEPAPER

AN INTRODUCTION TO NLDFT MODELS FOR POROSITY CHARACTERIZATION

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Non-local density functional theory (NLDFT) models are used to determine the porosity of a sample – pore size and pore size distribution – from measured gas adsorption isotherms. Here we provide simple, easy-to-understand answers to frequently asked questions relating to this topic, supplying the background understanding needed for effective application of this powerful mathematical tool.

What is DFT? And NLDFT?

Density functional theory (DFT) is a mathematical method or tool used in quantum physics to determine an approximate solution to the Schrödinger equation for a multi-bodied system. Let's unpack that somewhat complex sentence to relate DFT to the practicalities of gas adsorption studies.

In simple terms, the solution of Schrödinger's equation is a probability function called a wave function that describes the likelihood of finding an electron in a certain location at a specific energy level. We can therefore use Schrödinger's equation to predict the structure and properties of solids, liquids and gases by solving it for different systems. DFT is a well-established, relatively efficient computational tool that provides an approximate solution. Offering a good trade-off between accuracy and computational cost it is used routinely to predict the properties of condensed matter.

There are two levels of the density functional theory: (i) quantum DFT, a computational quantum mechanical modeling method used to describe the electronic structure of atoms, molecules, and condensed phases in terms of electron density rather than wave functions (orbitals) and (ii) classical DFT for fluids, a molecular modeling method used to describe properties of fluid systems in terms of the fluid density. By the density of electrons or fluids, we mean the density profile as a function of dimension (x, y, z). The density profile for systems of electrons or fluids is obtained by minimization of the energy functional or grand potential functional and represents the structure of a system of electrons or fluids.

In gas adsorption, DFT is used to model the properties of the sorptive fluid, typically nitrogen, confined in porous solids [1-2].

Work to apply DFT to adsorption isotherms began in the 1980s with the work of Seaton et al. [3] who first proposed a procedure for determination of the pore size distribution of porous carbons from adsorption isotherms and a simple DFT model. In this procedure the pore size distribution is obtained as a solution of the adsorption integral equation. Specifically, the aim was to effectively describe the non-homogeneous fluid behavior associated with phase changes that occur when fluids are constrained by walls, capillaries and slits. Scientists from Micromeritics were pioneers in this area and worked extensively on improving the application of DFT around this time [4-6]. By 1993, those leading the way had recognized the superiority of using non-local density approximations, a refinement of DFT, for gas adsorption analysis, and the application of non-local DFT (NLDFT) progressed steadily from this time [6-7].

How are NLDFT models used to generate porosity data?

Gas adsorption isotherms are measured across a pressure range that can extend from low relative pressure up to the saturation pressure of the fluid, depending on the purpose of measurement. Surface area measurements are performed at relatively low pressures and the resulting isotherm is used to estimate the amount of gas associated with the formation of a monolayer of gas molecules across the surface of the sample. Higher relative pressures lead to gas condensation, with fine pores filling first, up to complete saturation of the sample, generating the data required for porosity characterization.

In models for the determination of porosity, NLDFT is applied to calculate the properties of the condensed sorptive fluid within the pore, notably fluid density, under representative conditions. These values are used along with an appropriate physical representation of

pore structure to generate theoretical isotherms for a specific material. For example, the one-dimensional infinite slit model, which assumes that pores are slits formed between infinite walls, is widely used for porous carbons. This process generates what is known as a kernel, a series of theoretical isotherms that indicate the

amount of gas adsorbed as a function of pore size and pressure, at a specific temperature (see figure 1).

Mathematically comparing these theoretical isotherms with experimentally measured isotherm determines the pore size of the sample. In practice this is a complex, mathematical fitting and regression process.

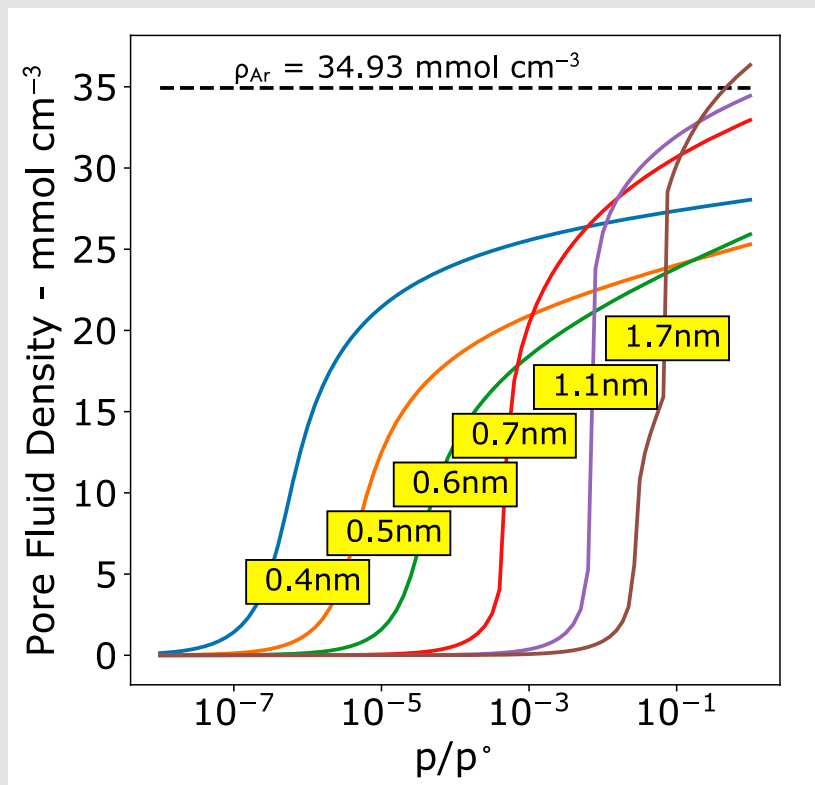
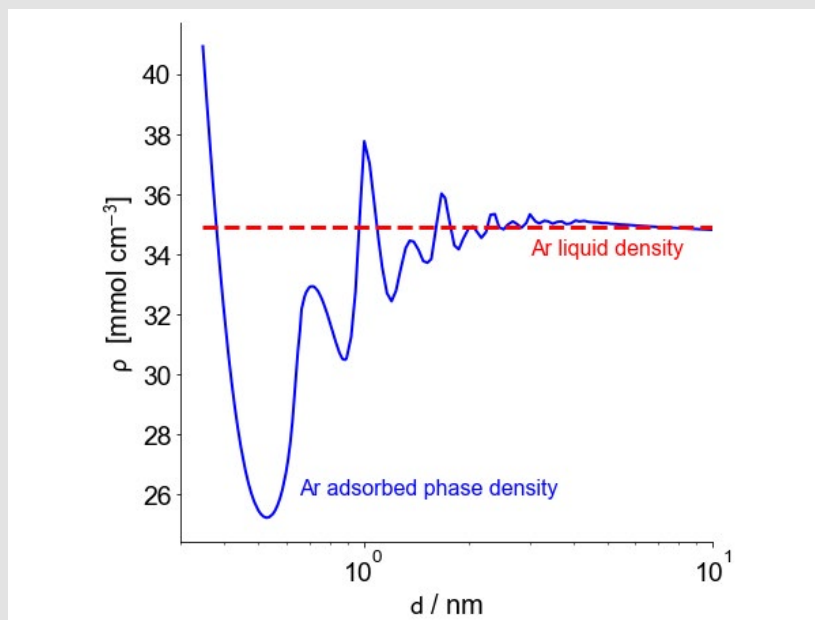


Figure 1: A kernel, a series of theoretical isotherms generated using an NLDFT model (left). Note how fluid density varies with pore size, an effect further illustrated for argon (below). At coarser pore sizes calculated density values converge to that of the bulk fluid.



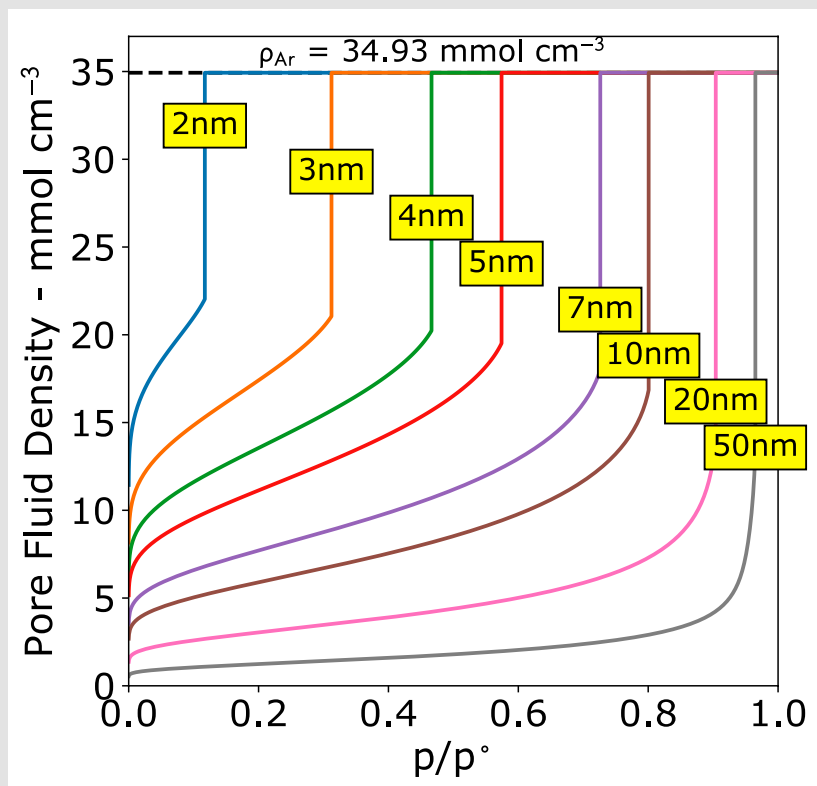


Figure 2: Model isotherms generated using BJH, which assumes that the condensed sorptive exhibits the same density as that of the bulk fluid and as a result is less accurate at finer pore sizes.

Why do I need an NLDFT model? Can't I use something simpler such as BJH?

The classic method of Barrett, Joyner and Halenda (BJH), which is underpinned by the Kelvin model of pore filling, is used widely for porosity characterization. It gives accurate results for many meso- and macroporous materials but has reduced precision under certain circumstances. An important limitation of the BJH method is that it cannot be applied to microporous materials.

The issue of reduced precision became apparent in the early 1990s when materials with well-defined porosity in the 2–8 nm range were first made in significant quantity. The BJH method fails to account for interactions between the pore surface and the sorptive fluid which become more significant at finer pore sizes (see figure 2). Such interactions change the properties of the fluid, particularly its density. Condensed nitrogen in a 2 or 3 nm pore does not exhibit typical bulk liquid-like behavior and a more complex model of fluid behavior is required to determine porosity with any accuracy.

Uniquely microporous materials, those with a pore size of less than 2 nm, can be described using for example, the Horvath-Kawazoe method. However, applying these methods in combination with BJH does not provide a continuous pore size distribution.

The defining attraction of NLDFT models is that they can be used to characterize materials that have porosity across three orders of magnitude, that extends from the micro- through to the meso- and macroporous region. Industrially important examples of such materials include activated carbons and zeolites. For materials such as these, NLDFT provides a single model that can extract a continuous pore size distribution to accurately quantify the complete porosity profile of the material.

So, NLDFT modelling is not needed for all materials?

That's right. BJH or other classic methods will work well for many materials.

In recent years gas adsorption equipment has become progressively more precise and adsorption isotherms can now be measured with extremely high resolution.

At the same time the ability to synthesize materials with closely controlled porosity has also improved steadily. As a result, we are now able to more effectively detect problems with simpler models to establish requirements for NLDFT. New and better core NLDFT models are introduced on a regular basis and the number of kernels available is also increasing, answering to identified needs.

Examples of materials for which NLDFT models are particularly helpful include: metal-organic frameworks (MOFs), carbons, oxides, carbon nanotubes and zeolites.

If I do need to apply an NLDFT model, then how do I do that in practice?

In practice, application of an NDLFT model is handled by the software of an appropriately specified gas adsorption system. There are two stages to the process.

The first step is selection of an appropriate model for the material being analyzed. Obviously, vendors differ with respect to the library of models they offer and the extent to which they invest in developing new models, so it is important to assess what's available if this is going to be an important feature of a new system, for your applications.

The second step is fitting of the model to the experimental data, a far from trivial mathematical process. Micromeritics systems offer powerful [8] software for the application of NLDFT including the SAIEUS program (Solution of Adsorption Integral Equation Using Splines) which can be used in conjunction with automatic or user-selected conditions to generate smooth, noise-free pore size distributions. A demo version and information about the full version of the SAIEUS program are available at www.NLDFT.com.

And when it comes to selecting a NLDFT model, how do they vary?

As we've already discussed it is crucial to choose a model/kernel that accurately represents the material of interest. NLDFT models are very much a work in progress as understanding grows and computing advances make new approaches tractable.

For example, efforts to improve on the one-dimensional infinite slit model, widely used for carbon, have shown that a simple two-dimensional model based on slit pores with parallel discs generates results that are in much closer agreement with experimental data [9]. Further modeling refinements that have proven successful include the introduction of energetic heterogeneity or geometric corrugation to the surface of the pore walls [10]. Introduction of the specific characteristics of the surface became possible with the application of 2D-NLDFT modeling. This latter modification eliminates certain artefacts associated with the use of standard NLDFT models thereby significantly reducing the standard deviations of fit associated with pore size distribution generation. The 2D-NLDFT models are considered second generation kernels [11] differentiating them from those generated using standard models.

For years, the characterization of carbon pore size distribution has been dominated by the analysis of nitrogen isotherms. The drawback of using nitrogen is its significant quadrupole moment that may interact with polar surface sites and affect the isotherm measurements. Recently, new 2D-NLDFT models were introduced [12-13] for the analysis of isotherms of oxygen and hydrogen. These gases have much lower quadrupole moments than nitrogen and thus are more appropriate for pore size distribution analysis.

To our knowledge, 2D-NLDFT kernels are currently only provided by Micromeritics via the MicroActive and SAIEUS programs.

In conclusion

NLDFT modelling is a complex topic with plenty of background reading available for those looking to find out more. On the other hand, when it comes to the practicalities of applying NLDFT models the key points to remember are relatively straight forward:

- NLDFT models are important for optimizing the value and application of gas adsorption for porosity characterization, particularly for analyzing materials that have structure that extends from the microporous into the meso- and macroporous region.
- If you are analyzing materials that need an NLDFT model, then look for a system that makes it easy to access and apply a relevant kernel. You don't need to be an expert theoretical physicist to use NLDFT modelling, you need a system that makes it easy to access and use models that will accurately represent your material.
- Not all vendors invest equally in NLDFT modelling and making the most up-to-date models available to customers. If this is a capability that is important to you then check out a company's credentials in this highly theoretical, but directly valuable area.

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Further reading:

To find out more about NLDFT and its evolution over the last decade please refer to the following bibliography.

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