

IMPROVED MODEL OF ACTIVATED CARBONS USING MOLECULAR SIMULATION

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Introduction

Non-graphitic carbons possess remarkable adsorption properties for non-polar molecules owing to their highly microporous structure. Subsequently these carbons have been exploited vigorously in a wide range of industrial applications. However the development of a systematic characterization of non-graphic carbons has proven to be a challenge. Due to an assortment of raw materials and a large range of production variables, industrially produced carbons exhibit widely differing properties. These differences are presumed to result from differences in structure. Hence an adequate characterization of carbonaceous materials must be versatile in its means of structural representation.

Methods

We propose here a model of activated carbon based on molecular simulation. The main goal of our model is to more accurately describe the true micro-structure of industrial carbons. Existing models generally assume activated carbons as being made up of small microcrystals composed of carbon basal planes of varying size (typically 2-5 nm). However these models do not adequately account for the relative variation in the basal plane alignment. Likewise, these models are rather idealized representations that are typically used to characterize industrial carbon structures after the fact—rather than implicitly incorporating the carbon structure in the development of the model.

We have constructed a modeling scheme based on the reverse Monte-Carlo (RMC) method [1-3]. We start with some fixed distribution of randomly generated idealized basal planes in a periodic, cubic simulation cell. Then through a series of random translational and rotational trial steps, we gradually allow the carbon basal planes to realign. The acceptance criteria for a given move is the requirement that the simulated carbon radial distribution function, $g_{new}(r)$, after the move more closely matches the experimental function, $g_{exp}(r)$, than the radial distribution function before the move, $g_{old}(r)$.

We also include as trial steps the random creation and annihilation of aromatic 6-fold rings along the

boarder of the rigid carbon basal planes. This redistribution of carbon is important in order to adequately represent the contributions to $g(r)$ due to the hexagonal arrangement of carbon within the aromatic rings.

Results and Discussion

In practice, the experimental radial distribution function can be obtained through small angle x-ray scattering (SAXS) and neutron scattering data. However as a test of our method, we generated a sample $g_{exp}(r)$ by starting with a random distribution of basal planes and relaxing the structure through canonical molecular dynamics. We then generated $g_{exp}(r)$ through statistical averaging of the radial distribution histogram in a canonical molecular dynamics simulation over 2 ms at 300K. The resulting carbon had a density of $1.07g/cm^3$ and was composed of basal planes containing a distribution of ring numbers (mean= 16.84, $\sigma = 4.17$). We used the above $g_{exp}(r)$ as input for the RMC scheme described above.

Figure 1 shows the dependence of the mean-square deviation in $g(r)$ defined by

$$\chi^2 \equiv \sum_{i=1}^N (g_{new}(r_i) - g_{exp}(r_i))^2$$

as a function of the number of RMC steps (defined as 1000 translation/rotation trials and 100 creation/annihilation trials). Adequate convergence in the radial distribution function is seen to occur after 100 RMC steps. The converged radial distribution function (dotted line in Figure 2) shows very little structural difference from $g_{exp}(r)$ (solid line).

Conclusions

We have demonstrated the the RMC methodology can be used to generate an activated carbon model that structurally represents the radial distribution function from experimental input. Such a model can be used to estimate a number of properties characteristic of the given carbon—for example: (micro)pore size distribution, (micro)pore volume, and adsorption isotherm.

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References

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Figure 1. Mean square deviation of $g(r)$.

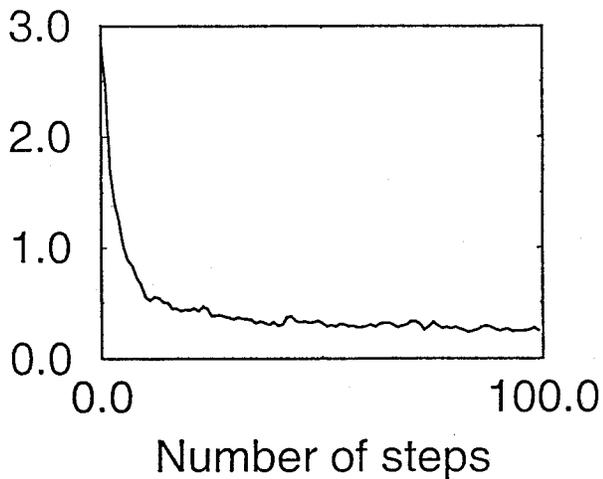
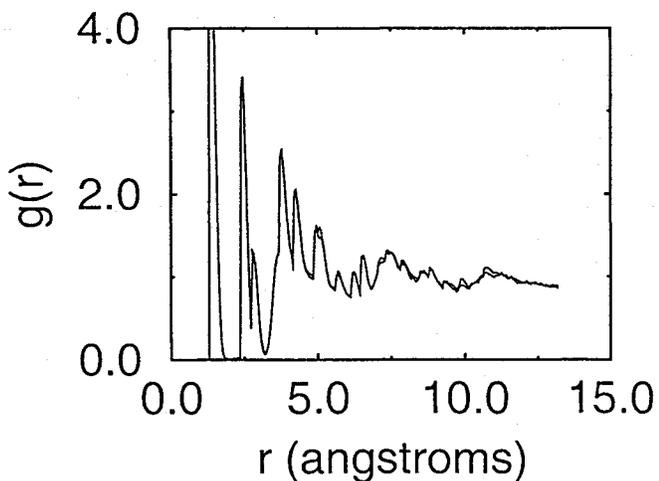


Figure 2. Radial distribution functions.



Solid line represents $g_{exp}(r)$. Dotted line represents converged distribution function $g(r)$.