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Freezing behavior in porous materials: Theory and experiment

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We report both experimental measurements and molecular simulations of the melting and freezing behavior of simple fluids in porous media. The experimental studies are for carbon tetrachloride and nitrobenzene in controlled pore glass (CPG), Vycor and activated carbon fibers (ACF). Differential scanning calorimetry (DSC) was used to determine the melting point in these porous materials. In the case of nitrobenzene (which has a dipole moment), dielectric spectroscopy was also used to determine melting points. Measurements by the two methods were in excellent agreement. The melting point was found to be depressed relative to the bulk value for both fluids in the silica based pores. While nitrobenzene in ACF showed a very small shift in melting temperature, a large increase in the melting temperatures was found for CCl₄ in ACF's, relative to the bulk. With the exception of the smallest pores, the melting point depression was proportional to the reciprocal of the pore diameter, in agreement with the Gibbs-Thomson equation. Structural information about the different confined phases was obtained by measuring the dielectric relaxation times using dielectric relaxation spectroscopy.

Monte Carlo simulations were used to determine the shift in the melting point, T_m , for simple fluids in pores having repulsive, weakly attractive and strongly attractive walls chosen to model a range of porous materials from silica based pores to carbon based pores, in terms of energy of the fluid-wall interaction. The strength of the interaction of the fluid with the pore wall is shown to have a large effect on the shift in T_m , with T_m being

reduced for weakly attracting walls. For strongly attracting walls, such as graphitic carbon, the melting point increases for slit-shaped pores. These trends are compared with the experimental trends for different fluids confined in different porous materials based on corresponding states theory. A new method for calculating the free energies of solids in pores based on Landau theory is used, and it is shown that the solid-liquid transition remains first order in these confined systems.

1. INTRODUCTION

Recently there has been growing interest in the study of fluid-solid transitions in porous materials. Important questions are the nature of the phase transition (first order vs. continuous), the direction of shift in the melting temperature T_m , nature and origin of hysteresis, dimensionality cross-over due to increasing confinement, structural changes of the condensed phases in the restricted pore geometries, effect on latent heats, etc. Improved understanding of confinement effects on freezing are essential in areas relating to lubrication, adhesion, fabrication of nanomaterials and nanotribology. In addition, these studies can provide insight into mechanisms involved in frost heaving and distribution of pollutants in soil. Freezing in porous media has also been widely employed in the characterization of porous materials using the method of thermoporometry. Some other possible applications are in the development of novel materials for energy storage, high speed vehicles and aircraft braking systems [1,2].

Experiments on freezing that have used porous silica glass as the confinement medium have always resulted in a decrease in the freezing temperature, T_{t} , as compared to the bulk. Freezing of oxygen in sol-gel glasses was studied by Warnock et. al. [3] by a sub-pico second optical technique. In this method, birefringence in optical pump pulses caused by the rotational motion of the molecules in the liquid was used to measure the subsequent molecular orientational relaxation time. A change in the value of the relaxation time provided an indication of the freezing temperature. The freezing temperature in the confined system was always depressed as compared to the bulk; the shift was larger for smaller pores, and as large as 10 K for the smallest (20 nm) pore. Unruh and co-workers [4] examined the melting behavior of indium metal in porous silica glasses by differential scanning calorimetry (DSC) measurements, and reported a large depression in melting point due to confinement. In view of the large body of experimental evidence for a decrease in the freezing temperature due to confinement ([5] and the refs. therein), it is tempting to assume that a decrease always occurs. However, a classical thermodynamic argument based on simple capillary theory determines the freezing temperature as the point at which the chemical potential of the solid core inside the pore equals that of the surround-ing fluid (for example, see ref. [5]),

$$\frac{\Delta T_f}{T_{fb}} = -2 \frac{(\gamma_{ws} - \gamma_{wl})\nu}{H\lambda_{fb}} \tag{1}$$

where T_{th} is the bulk freezing temperature, γ_{ws} and γ_{wl} are the corresponding wall-solid and wall-fluid surface tensions, v is the molar volume of the liquid, λ_{μ} is the latent heat of melting in the bulk and H is the pore width. Equation (1) is sometimes referred to as the Gibbs-Thomson equation, and predicts that the sign of $\Delta T_f = T_f - T_{fb}$ depends on whether γ_{ws} is greater or less than γ_{wl} . In a subsequent molecular simulation study of the effect of confinement on freezing of simple fluids in slit pores by Miyahara and Gubbins [6], it was shown that T_{f} was strongly affected by the strength of the attractive forces between the fluid molecules and the pore walls. For repulsive or weakly attractive potentials, the shift in the freezing temperature ΔT_f was negative. For strongly attracting walls such as carbons, an *increase* in T_f was observed. Thus, Miyahara and Gubbins explained the disparate experimental trends on the direction of the shift in the freezing temperature and provided the connection to the Gibbs-Thomson equation. The predictions of Miyahara and Gubbins were confirmed by free energy studies that provided the thermodynamic freezing temperature in confined systems; these studies established that the freezing transition remained first order despite the varied dimensionality [7,8].

In this article, we report a systematic study of the effect of the strength of the pore wall interaction on the phase behavior and molecular structure associated with melting and freezing. The DSC and dielectric spectroscopy experiments involving porous glasses and ACF's were performed at Adama Mickiewicza University, Poznan, Poland, and Chiba University, Chiba, Japan and the molecular simulations were performed at North Carolina State University, USA.

2. METHODS

Differential Scanning Calorimetry. Perkin-Elmer and Dupont thermal analyzers were used to determine the melting temperatures and latent heats of fusion, by measuring the heat released in the melting of nitrobenzene and CCl₄ in the bulk as well as in the porous silica and activated carbon fibers. Temperature scanning rates of 0.5-2 K/min were used in the experiments. The background of each raw DSC spectrum was subtracted from the signal, based on a second-

order polynomial fit to the measured heat flow. The melting temperatures were determined from the position of the peaks of the heat flow signals and the latent heats were determined based on the scaled area under these signals. The melting temperatures were reproducible to within 0.5° C for larger pores (≥ 25 nm); uncertainties were larger for the smaller pores. These uncertainties are a result of the width of the DSC peaks, which derive in part from variations in pore size, and geometry, and from the existence of metastable states. The latent heats were reproducible to within an accuracy of 5%.

Dielectric relaxation spectroscopy. The relative permittivity of a medium, $\kappa^* = \kappa' - i\kappa''$, is in general a complex quantity whose real part κ' (also known as the dielectric constant) is associated with the increase in capacitance due to the introduction of the dielectric. The imaginary component κ'' is associated with mechanisms that contribute to energy dissipation in the system, due to viscous damping of the rotational motion of the dipolar molecules in alternating fields. The latter effect is frequency dependent. The experimental setup consisted of a parallel plate capacitor of empty capacitance $C_0 = 4.2$ pF. The capacitance, C, and the tangent loss, $\tan(\delta)$, of the capacitor filled with nitrobenzene between the plates were measured using a Solartron 1260 gain impedance analyzer, in the frequency range 1 Hz - 10 MHz, for various temperatures. For the case of nitrobenzene in porous silica, the sample was introduced between the capacitor plates as a suspension of 200 μ m mesh porous silica particles in pure nitrobenzene. The contributions to κ^* were determined from,

$$\kappa' = \frac{C}{C_0}; \quad \kappa'' = \frac{\tan(\delta)}{\kappa'} \tag{2}$$

In equation (2), C is the capacitance, C_0 is the capacitance without the dielectric and δ is the angle by which current leads the voltage. Nitrobenzene was confined in porous silica (CPG and VYCOR), of pore widths H = 50 nm to 4 nm at 1 atm. pressure. The freezing temperature in the bulk is 5.6° C (the liquid freezes to a monoclinic crystal). $\kappa^* = \kappa' - i\kappa''$, the complex dielectric permittivity, is measured as a function of temperature and frequency.

For an isolated dipole rotating under an oscillating electric field in a viscous medium, the Debye dispersion relation is derived using classical mechanics,

$$\kappa^* = \kappa'_{\infty} + \frac{\kappa'_s - \kappa'_{\infty}}{1 + i\omega\tau} \tag{3}$$

In equation (3), ω is the frequency of the applied potential and τ is the orientational (rotational) relaxation time of a dipolar molecule. The subscript s re-

fers to static permittivity (low frequency limit, when the dipoles have sufficient time to be in phase with the applied field). The subscript ∞ refers to the optical permittivity (high frequency limit) and is a measure of the induced component of the permittivity. The dielectric constant is a natural choice of order parameter to study freezing of dipolar liquids, because of the large change in the orientational polarizability between the liquid and solid phases. The dielectric relaxation time was calculated by fitting the dispersion spectrum of the complex permittivity near resonance to the Debye model of orientational relaxation.

Simulation. We performed Grand Canonical Monte Carlo (GCMC) simulations of Lennard-Jones fluids adsorbed in regular slit shaped pores of different pore widths H and varying fluid-wall strengths. Here H is the distance separating the planes through the centers of the surface-layer atoms on opposing pore walls. The interaction between the adsorbed fluid molecules is modeled using the Lennard-Jones (12,6) potential with size and energy parameters chosen to describe methane and CCl₄ [8,9]. The fluid-wall interaction is modeled using a "10-4-3" Steele potential [10],

$$\phi_{fw}(z) = 2\pi\rho_w \varepsilon_{fw} \sigma_{fw}^2 \Delta \left[\frac{2}{5} \left(\frac{\sigma_{fw}}{z} \right)^{10} - \left(\frac{\sigma_{fw}}{z} \right)^4 - \left(\frac{\sigma_{fw}^4}{3\Delta(z+0.61\Delta)^3} \right) \right]$$
(4)

Here, the σ 's and ε 's are the size and energy parameters in the LJ potential, the subscripts f and w denote fluid and wall respectively, z is the coordinate perpendicular to the pore walls and k_{g} is the Boltzmann's constant. The fluidwall interaction energy parameters corresponding to a graphite pore were taken from Ref. [10]. For a given pore width H, the total potential energy from both walls is given by,

$$\phi_{pore}(z) = \phi_{fw}(z) + \phi_{fw}(H - z)$$
(5)

The strength of the fluid wall interaction is determined by the parameter $\alpha = 2\pi\rho_w\varepsilon_{jw}\sigma_{jw}^{*}\Delta$. For example, in the case of methane, $\alpha = 0$ corresponds to a purely repulsive or hard wall, $\alpha = 0.76\varepsilon_{ff}$ corresponds to a weakly attractive wall and $\alpha = 2.0\varepsilon_{ff}$ corresponds to a strongly attractive graphite wall.

The simulation runs were performed in the grand canonical ensemble, fixing the chemical potential μ , the volume V of the pore and the temperature T. The system typically consisted of 600-700 adsorbed molecules. For the case of attractive pore-wall interaction, the adsorbed molecules formed distinct layers parallel to the plane of the pore walls. A rectilinear simulation cell of $10\sigma_{ff}$ by $10\sigma_{ff}$ in the plane parallel to the pore walls was used, consistent with a cutoff of $5\sigma_{ff}$ for the fluid-fluid interaction. The simulation was set up such that insertion, deletion and displacement moves were attempted with equal probability, and the displacement step was adjusted to have a 50% probability of acceptance. Thermodynamic properties were averaged over 100-500 million individual Monte Carlo steps. The length of the simulation was adjusted such that a minimum of fifty times the average number of particles in the system would be inserted and deleted during a single simulation run.

Free energy method. The method relies on the calculation of the Landau free energy as a function of an effective bond orientational order parameter Φ , using GCMC simulations [8]. The Landau free energy Λ is defined by,

$$\Lambda[\Phi] = -k_{B}T\ln(P[\Phi]) + \text{constant}$$
(6)

where $P[\Phi]$ is the probability of observing the system having an order parameter value between Φ and $\Phi + \delta \Phi$. The probability distribution function $P[\Phi]$ is calculated in a GCMC simulation as a histogram, with the help of umbrella sampling. The grand free energy Ω is then related to the Landau free energy by

$$\exp(-\beta\Omega) = \int d\Phi \exp(-\beta\Lambda[\Phi])$$
(7)

The grand free energy at a particular temperature can be calculated by numerically integrating equation (7) over the order parameter space. We use a twodimensional order parameter to characterize the order in each of the molecular layers.

$$\Phi_{j} = \left| \frac{1}{N_{b}} \sum_{k=1}^{N_{b}} \exp(i6\theta_{k}) \right| = \left| \left\langle \exp(i6\theta_{k}) \right\rangle_{j} \right|$$
(8)

 Φ_j measures the hexagonal bond order within each layer j. Each nearest neighbor bond has a particular orientation in the plane of the given layer, and is described by the polar coordinate θ . The index k runs over the total number of nearest neighbor bonds N_b in layer j. The overall order parameter Φ is an average of the hexagonal order in all the layers. We expect $\Phi_j = 0$ when layer j has the structure of a two-dimensional liquid, $\Phi_j = 1$ in the crystal phase and $0 < \Phi_j < 1$ in an orientationally ordered layer.

3. RESULTS

3.1. Experiments and Simulations on Porous Silica

DSC & Dielectric Spectroscopy. DSC scans corresponding to melting of nitrobenzene are shown in Figure 1a. The deep minimum at 5.6° C that is independent of pore size corresponds to the melting of the bulk nitrobenzene in which the porous particles are suspended. In addition, a second minimum that is dependent on the pore size is also observed. This signal corresponds to the melting of nitrobenzene in the pores, and shifts to lower temperatures as the pore size is reduced.

The capacitance C and tangent loss $tan(\delta)$ were measured as a function of frequency and temperature for bulk nitrobenzene and for nitrobenzene adsorbed in CPG and Vycor glass of different pore sizes ranging from 50 nm to 4.0 nm. The typical behavior of κ' vs. T is shown in Figure 1b. For pure, bulk nitrobenzene, there is a sharp increase in κ' at $T = 5.6^{\circ}$ C, corresponding to the melting point of the pure substance. For nitrobenzene confined in CPG, the sample is introduced as a suspension of nitrobenzene filled CPG particles in pure nitrobenzene, between the capacitor plates. The capacitance measurement vielded an effective value of the relative permittivity of the suspension of CPG in pure nitrobenzene. Thus κ' shows two sudden changes. The increase that depends on pore size is attributed to melting in the pores, while the increase at 5.6° C corresponds to the bulk melting. The shifts in the melting temperature obtained using both DSC and dielectric spectroscopy (DS) measurements are in good agreement and vary linearly with the reciprocal pore width for large pores [5]. The deviations from linearity, and hence from the Gibbs-Thomson equation, are appreciable at pore widths as small as 4.0 nm. The DSC scans for CCl4 melting in porous silica showed similar trends to the melting of nitrobenzene (see Figure 5(b)).



Figure 1. (a) Representative DSC scans for melting of nitrobenzene in CPG, after subtraction of background signal. Results are for: bulk nitrobenzene, and for CPG samples of mean pore size 50 nm, 25 nm and 7.5 nm. Each scan is shifted in vertical scale by 10 mW for the sake of clarity. (b) Relative permittivity, κ' for nitrobenzene in porous silica, as a function of temperature for different pore widths

The spectrum of the complex permittivity (κ', κ'' vs. ω) is fit to the dispersion relation (equation (3)), to determine the dielectric relaxation time τ . which gives valuable information about the structure of the condensed phase. The frequency range in this study is expected to encompass the resonant frequencies corresponding to the dielectric relaxation in the solid phases. To probe the liquid relaxation behavior would require a frequency range that is 4 to 5 orders of magnitude higher. The spectrum plots for nitrobenzene in a 7.5 nm CPG at temperatures below the freezing temperature in the pore show a Debye type relaxation with a single time scale that is estimated to be $\tau = 1.44$ ms. At temperatures above the pore melting temperature, (e.g., see Figure 2 at T = -4°C), the behavior is significantly different. From the double peak structure of the $\kappa''(\omega)$ and the double inflection in the $\kappa'(\omega)$ curve, two different dielectric relaxation times are calculated. There is a shorter relaxation time $\tau_1 = 43.6 \,\mu s$, in addition to the longer component $\tau_2 = 1.7 \,\mu s$. The longer component relaxation, $\tau_2 = 1.7$ ms, is attributed to the bulk crystalline phase of nitrobenzene. The shorter relaxation component, $\tau_1 = 43.6 \,\mu s$, is attributed to the molecular dynamics of the contact layer. The dispersion corresponding to the nitrobenzene molecules in the liquid phase occurs in a frequency range that is much higher than measured in this study.



Figure 2. Spectrum plot for nitrobenzene in a 7.5 nm pore at $T = -4^{\circ}$ C; this plot yields two distinct dielectric absorption regions. The solid and the dotted curves are fits to the Debye dispersion relation

Simulation. The Landau free energy calculations showed that for the case of LJ methane and CCl₄ confined in hard walled and weakly attractive slit pores, $\alpha < 0.85\varepsilon_{ff}$, the freezing temperature in the pore was depressed compared to the bulk. For most liquids confined in silica based pores the α values fall in the range of the weakly attractive pores [11]. This behavior is consistent with the trends observed in the literature and with the Gibbs-Thomson equation. For the case of a hard wall pore, the confined system exists as either a liquid or a solid.

For a weakly attractive pore that mimics nitrobenzene in silica, the free energy surface in Figure 3(a) shows the presence of three phases. Phase A is the liquid phase and Phase C is the crystal phase. An intermediate phase B also exists, whose structure is plotted in Figure 3(b). The plots represent two-dimensional, in-plane pair correlation functions in each of the molecular layers. The pair correlation function of the contact layer (the layer adjacent to the pore walls) is isotropic, representing a liquid-like layer, while the pair correlation functions for the inner layers show a broken translational symmetry corresponding to a 2d crystalline phase; for this system the contact layers freeze at a temperature below that of the inner layers. The existence of such a contact layer phase with different thermodynamic and structural properties compared to the inner layers is consistent with the experimental measurements of the dielectric relaxation times for nitrobenzene in CPG and VYCOR.



Figure 3. (a) The Landau free energy for LJ nitrobenzene confined in a model silica pore. The three minima correspond to three different phases. (b) The structure of phase B, showing that the contact layer is a fluid while the inner layers are frozen

3.2. Experiments and Simulations on Carbons

DSC. The evolution in the DSC patterns of different CCl₄-ACF samples obtained during melting and freezing runs has been studied by Watanabe et al. [12]. The positions of the peaks in the DSC spectrum were found to be independent of the temperature scanning rate in the range 1.0 to 5 Kmin.⁻¹. The scan for bulk CCl₄ showed three ``exothermic" peaks at 242 K, 228 K and 218 K corresponding to liquid to metastable fcc-solid phase, fcc to rhombohedral phase and rhombohedral to monoclinic phase respectively. The observed transitions are systematically shifted by 10 K compared to the values found in the literature because of supercooling achieved during the freezing run. Freezing/melting in the confined system occurs at 299 K; the peak positions in each of the DSC scans for melting and freezing runs corresponding to CCl₄ confined in three different samples of ACF (P5 with H = 1.1 nm, P10 with H = 1.4 nm and P20 with H = 1.8 nm) showed an *upward* temperature shift of 57 K. Unlike the prediction by the Gibbs-Thomson equation, the freezing temperature is found to be independent of pore width in the micropore regime (H = 1.0-1.8 nm); see Figure 5. The enthalpies of freezing for the confined system, calculated from the peak areas were found to be 1.0 % of the bulk values [12]. The nature of the solid phase cannot be determined by DSC experiments alone. However, the peaks corresponding to the solid-solid transitions that take place in the bulk are absent in the confined system.

Simulation. The Landau free energy calculation for LJ CCl₄ in ACF's were performed for a range of pore sizes. For pore widths that accommodate one to three confined CCl₄ layers, it was found that all the layers froze in unison at the freezing temperature, and that this temperature was much higher than the bulk freezing temperature of LJ CCl₄. For pore widths that accommodate four or more layers of adsorbate, it was found that the contact layers froze at a higher temperature than the inner layers which in turn froze at a temperature above the bulk freezing temperature. The Landau free energy formulation provided the means to calculate both transition temperatures. Each Landau free energy curve at a particular temperature (see Figure 4) showed a triple-well structure (with three minima), corresponding to (1) a phase with isotropic fluid sture within each layer, (2) a phase with frozen contact layer (the inner layers being fluid-like) and (3) a phase with all the layers having the structure of a 2-d hexagonal crystal.



Figure 4. (a) The Landau free energy for CCl_4 confined in a model graphite pore. (b) The structure of phase B showing that the contact layer is frozen, while the inner layers remain fluid-like

The cross-over of the grand free energy functions for each phase gave the thermodynamic freezing temperature of the contact layers and the inner layers. The freezing temperatures of the contact and the inner layers for the various pore widths are shown in Figure 5(a).

4. DISCUSSION

The melting point of nitrobenzene and CCl_4 in the silica pores is always depressed (Figure 5(b)), due to the rather weak interaction of the fluid molecules with the pore walls. The linear relationship between the shift in the pore melting temperature and the inverse pore diameter is consistent with the Gibbs-Thomson equation for larger pore sizes . The deviations from linearity, and hence from the Gibbs-Thomson equation are appreciable at pore widths as small as 4.0 nm, however. The quantitative estimates of the rotational relaxation times in the fluid and crystal phases of confined nitrobenzene support the existence of a contact layer with dynamic and structural properties different than the inner layers. The Landau free energy calculation for the simple model that mimicked the weak silica wall interaction confirmed the existence of such a contact layer with different structural properties.



Figure 5. (a) Freezing temperatures of the contact layers and the inner layers for LJ CCl₄ confined in ACF slit pores of different pore widths, calculated using the Landau free energy method. (b) The shift in the freezing temperature of CCl₄, $\Delta T = T_f - T_{fb}$ as a function of pore width, in different porous materials obtained from simulation and experiment

The importance of the strength of the fluid wall interaction on the nature of the shift in the freezing tempreature of fluids in confined systems is shown in Figure 5(b). As opposed to the silica based pores, the CCl_4 molecules experi-

ence an elevation in the freezing tempreature when confined in the graphite based pores of the activated carbon fibers, consistent with the strong interaction potential between the CCl₄ molecules and graphite. The comparison of the DSC results and the simulation (Figure 5(b)) shows that the simplified model of spherical LJ CCl₄ and regular slit shaped graphite pore with smooth walls captures the plateau in the $\Delta T(H)$ function; however it overestimates the shift in the freezing temperature. In this regime, ΔT is 60 K in the experiments and is about 90 K in the simulation. The overestimation of the freezing temperature shift in the simulation is a reflection of the simplicity of the model used. It is easier for spherical molecules in slit pores to freeze when compared to five-site LJ tetrahedral molecules (a more realistic representation of CCl₄) in a real activated carbon with a more disordered pore structure. More realistic fluid-fluid potential models based on site-site LJ interactions could lead to an improvement in the prediction of the simulation results, as could a more realistic model of the pore structure. The Gibbs-Thomson equation is valid when the effect of the contact layers are negligible on the inner layers. When the number of inner layers are comparable with the number of contact layers, a deviation from linear behavior (G-T regime) is observed. The freezing temperature in the "nonlinear" regime is influenced by the freezing of the contact layers [9].

Since we have calculated the freezing temperatures and the phase behavior (Landau free energies) as a function of the relative strengths of the fluid-wall and the fluid-fluid interaction, α/ε_{ff} , a global phase diagram can be constructed that can predict the freezing temperature shift and the phase behavior (for example the structure of the different phases in the system) for different fluids confined in different porous materials, based on corresponding states theory, as long as the interaction energies can be approximated by the LJ potential [11]. Such a phase diagram can be used as a guide to estimate freezing temperatures of different fluids in real porous materials. For example, in the case of nitrobenzene confined in ACF, the relative strength of the fluid-wall interaction to the fluid-fluid interaction α is $0.95\varepsilon_{\text{ff}}$, which corresponds to a neutral pore. Thus the corresponding states theory predicts the shift in the freezing temperature of this confined system to be close to 0 K [11]. The melting temperature of the real nitrobenzene in ACF is about 8°C, measured using dielectric relaxation spectroscopy. Thus, the shift is about 2°C, in excellent agreement with the predictions of the corresponding states theory [11]. Efforts are also underway to use more realistic fluid potentials and pore models in the simulation. Recently Gelb and Gubbins [13] proposed a novel mechanism to realistically model the formation and structure of porous silica glasses using spinodal decomposition of a binary fluid mixture in the two-phase liquid-liquid region. This model is known to closely represent the actual pore size distribution of real porous silica and incorporates complex pore networking. We plan to study freezing of simple fluids using the free energy method in such a pore model, and to make direct comparison with experimental results for CCl₄ in CPG. For the case of activated carbons, Thomson and Gubbins [14] have proposed an improvement over the slit pore model, by explicitly accounting for interactions between different graphene sheets. Their proposed model includes networking and polydispersity effects and reproduces the structure of the real porous material very closely.

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