

REMARKABLE FREEZING BEHAVIOR IN ACTIVATED CARBON FIBERS: COMPARISON BETWEEN SIMULATION AND EXPERIMENT

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Introduction

Experiments on freezing that have used porous silica glass as the confinement medium have always resulted in a decrease in the freezing temperature, T_f , as compared to the bulk [1]. Microporous activated carbon fibers are well characterized porous materials and serve as highly attractive adsorbents for simple non-polar molecules, the adsorbent-adsorbate interaction being mostly dispersive. Recent molecular simulation studies have predicted an *upward shift* in the freezing temperature ($\Delta T_f = T_{f,pore} - T_{f,bulk} > 0$) for simple fluids confined in such highly attractive carbon slit pores [2,3]. Our DSC experiments verify these predictions about the *increase* in T_f . The results also indicate significant deviation from the prediction of ΔT_f with pore width H , based on simple capillary theory. We also employ a recently developed free energy method to calculate the exact freezing temperature in confined systems using molecular simulation, in order to address the failure of the simple capillary theory.

Methods

Pitch-based activated carbon fibers (P5, P10 and P20) of different pore widths in the micropore region were used as adsorbent materials. CCl_4 was made to adsorb on dry ACF samples at 303 K under saturated vapor pressure. The DSC scans were performed at temperature scanning rates of 5.0–1.0 Kmin^{-1} using a MAC Science, DSC3100 calorimeter. The freezing and melting temperatures were measured by identifying the peak position in the DSC scans relative to the background

and the enthalpies of the phase change were calculated from the peak areas.

The simulation runs (GCMC) were performed in the grand canonical ensemble. The interaction between the adsorbed fluid molecules was modeled using the Lennard-Jones (12,6) potential with size and energy parameters chosen to describe CCl_4 . Activated carbon fibers were modeled as regular slit like graphite pores. For the fluid-wall interaction, an integrated “10-4-3” Steele potential was used. The free energies of the confined phases were calculated using a novel free energy method based on order parameter formulation [3]. The true (thermodynamic) freezing temperatures were inferred from the calculated free energies.

Results and Discussion

In figure 1 is shown the evolution in the DSC patterns of different CCl_4 -ACF samples obtained during melting and freezing runs. The peak position in each of the DSC scans for melting and freezing runs corresponding to CCl_4 confined in ACF's (P5, P10 and P20) indicates that freezing/melting in the confined system occurs at 299 K, showing 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 ($H = 1.0$ – 1.4 nm); see figure 2. The enthalpies of freezing for the confined system, calculated from the peak areas were found to be between 0.1 and 1.0 % of the bulk.

The Landau free energy calculation was performed for the different pore sizes. For pore widths

that accommodate one to three confined CCl_4 layers, it was found that all the layers froze in unison at a freezing temperature that was much higher than the bulk freezing temperature of LJ CCl_4 . However, for pore widths that accommodate four layers or more, it was found that the contact layers froze at a higher temperature compared to the inner layers. The Landau free energy formulation automatically led to the calculation of both transition temperatures. Each Landau free energy curve at a particular temperature had a triple-well structure (with three minima), each corresponding to one phase. The crossover of the grand free energy functions for each phase gave the thermodynamic freezing temperature of the contact layers and the inner layers [4].

The plot in figure 2 shows good agreement between the results of the simplified model of LJ CCl_4 and regular slit shaped graphite pore and experiment; in particular the model captures the plateau in the $\Delta T(H)$ function, however it overestimates the shift in the freezing temperature. The Gibbs-Thomson equation is valid when the effect of the contact layers are negligible on the inner layers. As the number of inner layers are comparable with the number of contact layers, a deviation from linear behavior (G-T regime) is observed followed by a cross-over to the plateau regime. The freezing temperature in the plateau regime is determined by the freezing of the contact layers [4].

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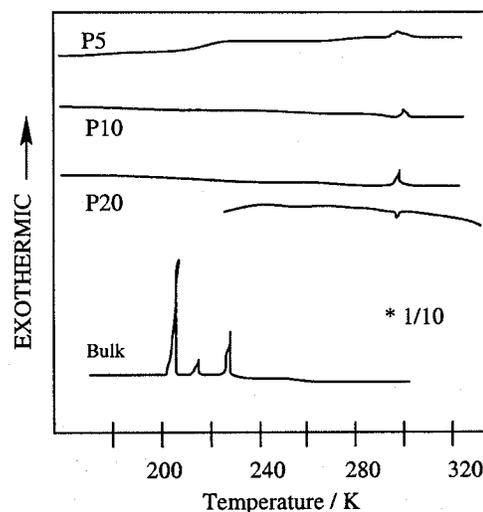


Fig 1: DSC scans for freezing of CCl_4 in the bulk and melting/freezing of CCl_4 confined in ACF's. DSC scan corresponding to a melting run is shown only for the case of the P20 ACF.

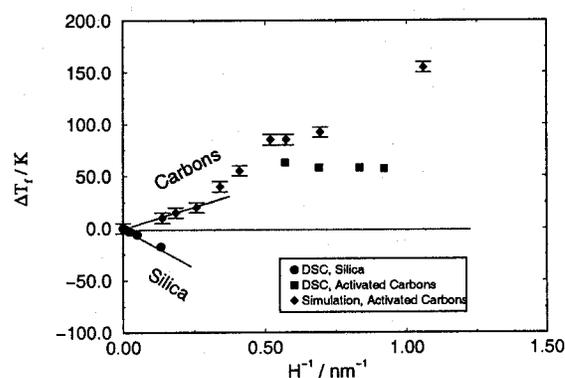


Fig 2: Comparison of the freezing temperatures between simulation and experiment. The results for activated carbons are from this study. The DSC results for silica are reproduced from ref. [1].