

An experimental study of melting of CCl₄ in carbon nanotubes

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We report dielectric relaxation spectroscopy measurements of the melting point of carbon tetrachloride confined within open-tip multi-walled carbon nanotubes with two different pore diameters, 4.0 and 2.8 nm. In both cases, a single transition temperature well above the bulk melting point was obtained for confined CCl₄. These results contrast with what was obtained in our previous measurements using carbon nanotubes with a pore diameter of 5.0 nm, where multiple transition temperatures both above and below the bulk melting point of CCl₄ were observed. Our experimental measurements are consistent with our recent molecular simulation results (F. R. Hung, B. Coasne, E. E. Santiso, K. E. Gubbins, F. R. Siperstein and M. Sliwinska-Bartkowiak, *J. Chem. Phys.*, 2005, **122**, 144706). Although the simulations overestimate the temperatures in which melting upon confinement occurs, both simulations and experiments suggest that all regions of adsorbate freeze at the same temperature, and that freezing occurs at higher temperatures upon reduction of the pore diameter.

Introduction

Freezing and melting of fluids confined in nanoporous materials have practical applications in adhesion, lubrication, characterization of porous materials, and nanofabrication. From a fundamental viewpoint, studies of freezing and melting of confined systems can provide important insights on the effect of confinement, surface forces and reduced dimensionality on the phase behavior of host molecules. A large amount of experimental evidence^{1–3} clearly indicates that the phase diagram of a substance can be significantly altered when confined within a porous material. Most of the early experimental studies,^{1,2} as well as recent works on freezing in confinement³ have been carried out using different siliceous materials (mainly MCM-41, SBA-15 and Vycor glass) and a wide variety of adsorbates, such as water,^{4–8} methyl chloride,⁹ methanol,¹⁰ nitrobenzene,^{11,12} aniline,¹³ carbon tetrachloride,¹¹ nitrogen,^{14,15} carbon monoxide,^{14–16} krypton,^{14,17} argon,^{16,18–20} carbon dioxide,²¹ oxygen,^{22,23} benzene,^{5,24–26} cyclohexane,^{5,24} and acetonitrile,²⁷ among others. Significant hysteresis effects between freezing and melting were observed, as well as evidence of different freezing behaviors for the adsorbate in the central regions of the pore and the contact layer (the adsorbed molecules adjacent to the pore wall), suggesting the presence of inhomogeneous confined phases (see, *e.g.* refs. 7, 15, 19, 25). In most cases, the structure of the confined solid was found to deviate from the bulk crystal phase, and the morphology of the confined solid was strongly dependent on the pore size. For instance, the confined material was found to crystallize only partially below certain pore sizes, and for even smaller pores an amorphous solid phase was always observed. All those studies indicate that the freezing temperature inside the weakly attrac-

tive silica pores is lower than that for the bulk. For pore sizes larger than 5 nm, the depression in the confined freezing temperature becomes larger as the pore size decreased, as predicted by the Gibbs–Thomson equation.^{1–3} This macroscopic equation was found to break down for systems confined in pores of small sizes, up to a few adsorbate molecular diameters,^{1–3} where the depression in the freezing temperature inside the pore becomes non-monotonically larger with reduction of the pore size.

In contrast, simulation and experimental studies have shown that an elevation in the freezing point is observed for systems where the adsorbate-wall interactions are strong compared to the adsorbate–adsorbate interactions. For instance, Klein and Kumacheva²⁸ studied cyclohexane and octamethylcyclotetrasiloxane (OMCTS) confined between parallel mica plates in a surface force apparatus (SFA). Upon reduction of the separation between the surfaces, it was observed that a sharp transition occurred at a certain pore width, and below this value the confined film could sustain a finite shear stress for macroscopic times, and the film rigidity (quantified by an “effective viscosity”) greatly increased. This was interpreted as a liquid to solid phase transition occurring at temperatures well above the bulk freezing point. In addition, a number of experiments using activated carbon fibers (ACF) have reported that the freezing temperature in confinement may be lower (water,^{29–31} octanol³² and undecanol³²) or higher (methanol,³¹ carbon tetrachloride,³³ benzene,³⁴ aniline,³⁵ OMCTS³⁶ and cyclohexane³⁶) than the bulk value; in some cases (nitrobenzene³⁷), no appreciable change in the freezing temperature was observed.

The previous results involved adsorbents with strongly attractive pores of slit-like geometry. Recently, Hung *et al.*³⁸ and Sliwinska-Bartkowiak *et al.*³⁹ reported dielectric relaxation spectroscopy results for the melting points of nitrobenzene and carbon tetrachloride, confined in open-tip multi-walled carbon nanotubes (MWCNT) with an internal diameter of 5.0 nm; the relaxation times of confined nitrobenzene were also

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reported. MWCNT are representative of materials with strongly attractive *cylindrical* pores. For both substances, transition temperatures were observed both above and below the bulk melting point. The results suggested the presence of inhomogeneous phases, composed of combinations of crystalline and liquid regions within the pore over extended temperature ranges. The experimental results for CCl₄ within carbon nanotubes were in good agreement with molecular simulation results.⁴⁰

In this paper we present an experimental study aimed at determining the effect of pore size on the melting points of CCl₄ when confined in open-tip multi-walled carbon nanotubes. The melting behavior of the adsorbate is investigated by means of dielectric relaxation spectroscopy measurements, and two different pore diameters were considered, 4.0 and 2.8 nm. We compare these experimental results with those previously obtained for MWCNT with a diameter of 5.0 nm,^{38,39} in addition, we also compare with molecular simulation results for CCl₄ within model MWCNT of similar diameters, 3.9 and 2.8 nm, which were reported in a previous publication.⁴⁰

Experimental method

In our experiments we have used purified multi-walled carbon nanotubes (MWCNT) from Nanocyl S.A. (Sambreville, Belgium). The samples were oxidized by a treatment with CO₂ to open the MWCNT tips. We have used two different samples with narrow pore size distributions and different average inner diameters, 4.0 and 2.8 nm; the latter consists of double-walled carbon nanotubes. The samples were characterized by means of transmission electron microscopy (TEM), scanning electron microscopy (SEM) and nitrogen adsorption measurements. The carbon nanotube samples were heated to 60 °C and kept under vacuum (10⁻³ torr) to remove traces of air and moisture prior to the introduction of carbon tetrachloride. The CCl₄ samples were reagent grade chemicals, and were distilled twice prior to their use in experiments. The conductivity of the purified CCl₄ samples was found to be less than 10⁻¹⁶ Ω⁻¹ m⁻¹.

Dielectric relaxation spectroscopy (DRS) was used to determine the experimental melting points of confined CCl₄. The experimental setup consisted of a parallel plate capacitor of empty capacitance $C_0 = 4.2$ pF. The capacitance C , and the tangent loss $\tan(\delta)$ (where δ is the angle by which current leads the voltage), of the capacitor filled with the sample was measured at different temperatures T and frequencies ω using a Solartron 1260 gain impedance analyzer, in the frequency range 1 Hz–1 MHz. The complex dielectric permittivity $\kappa^* = \kappa_r - i\kappa_i$ is related to the measured quantities by $\kappa_r = C/C_0$, $\kappa_i = \tan(\delta)/\kappa_r$.^{11,41} As a solid phase sample is heated, phase changes such as melting manifest themselves by changes in the C vs. T behavior. For the case of confined CCl₄, the sample was introduced between the capacitor plates as a suspension of CCl₄-filled carbon nanotubes in pure CCl₄; the measurement thus yields an effective capacitance for the sample (bulk and confined systems). During the experiments, the temperature of the sample was controlled with an accuracy of 0.1 K using a cryostat. A measurement of the relaxation times of CCl₄, which could have given information of the dynamics of the confined phase, was not attempted. The relaxation times for CCl₄ are considerably faster than those for polar molecules such as nitrobenzene, and thus only slow-dynamics processes such as MWS polarization and crystal relaxation would be detected. Moreover, the non-polar nature of CCl₄ produces weak signals in the experiments since the relaxations are mostly due to induced polarization (with frequencies in the range of GHz), rather than orientational polarizability effects, as is the case for polar fluids such as nitrobenzene. Further details of these experimental methods are described elsewhere.^{11,38,41}

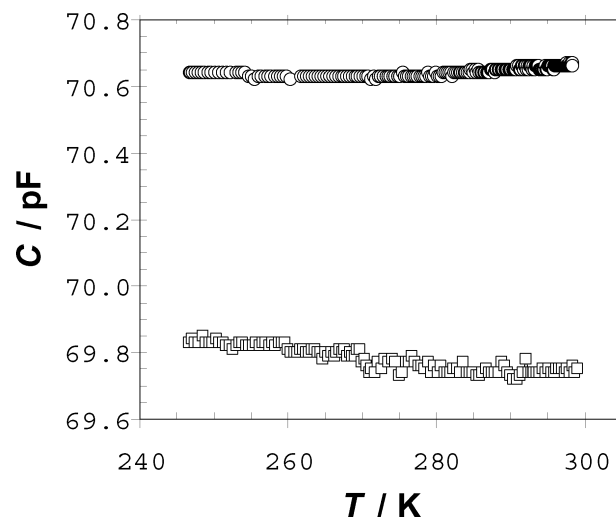


Fig. 1 Capacitance C as a function of temperature T for empty (no adsorbate), open-tip MWCNT, with an average internal pore diameter of 4.0 nm (circles) and 2.8 nm (squares). The measurements were performed at a frequency ω equal to 600 kHz. The error bars for the capacitance and temperature are equal to ± 0.01 pF and ± 0.1 K, respectively.

Results and discussion

In Fig. 1 we present experimental measurements of the capacitance C as a function of temperature T , for empty (no adsorbate), open-tip (pretreated with CO₂) MWCNT samples. A frequency $\omega = 600$ kHz was used in our measurements. These curves show negligible changes in C upon variations in T . In contrast, changes in the C vs. T behavior can be observed for CCl₄ confined within open-tip MWCNT with an internal diameter $D = 4.0$ nm (Fig. 2) and $D = 2.8$ nm (Fig. 3). We will first discuss the results obtained for $D = 4.0$ nm (Fig. 2). These results were obtained for two different frequencies $\omega = 100$ and 600 kHz. Our experiments started with a sample at $T = 110$ K, to ensure all CCl₄ is in the solid phase. Melting for both bulk and confined CCl₄ is observed in our experiments since the samples consist of a suspension of CCl₄-filled MWCNT in bulk CCl₄. Both curves exhibit a sharp jump that starts at $T \sim 226$ K. This transition corresponds to bulk CCl₄ undergoing a solid–solid transition between crystalline rhombohedral (Ib) and monoclinic (II) forms, which has been reported⁴² to occur at 225 K. As the temperature is increased, we observe a small

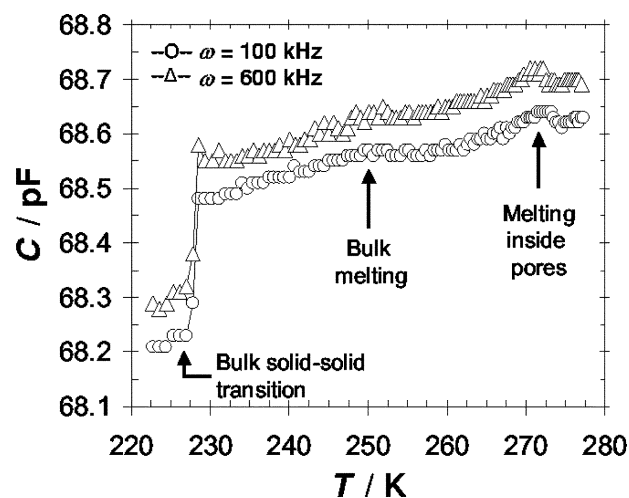


Fig. 2 Capacitance C as a function of temperature T for CCl₄ in open-tip MWCNT with an average internal pore diameter of 4.0 nm. The measurements were performed at frequencies ω equal to 100 kHz (circles) and 600 kHz (triangles). The error bars for the capacitance and temperature are equal to ± 0.01 pF and ± 0.1 K, respectively.

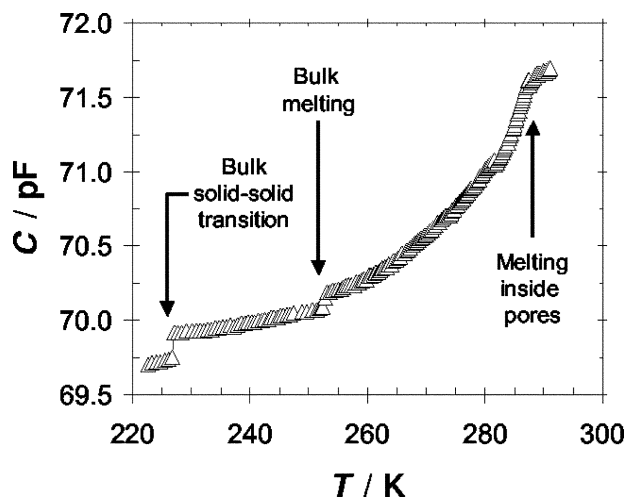


Fig. 3 Capacitance C as a function of temperature T for CCl_4 in open-tip MWCNT with an average internal pore diameter of 2.8 nm. The measurements were performed at frequencies ω equal to 600 kHz. The error bars for the capacitance and temperature are equal to ± 0.01 pF and ± 0.1 K, respectively.

“bump” whose maximum is located at $T \sim 250$ K, and is related to a change of density in the system. This feature should correspond to melting of bulk CCl_4 from a crystalline rhombohedral (Ib) phase to a liquid phase at 250 K.⁴² We observe a second “bump” whose maximum is at a much higher temperature, $T \sim 272$ K. This temperature does not correspond to any known transition for bulk CCl_4 , and therefore may represent melting of CCl_4 within the MWCNT. In support of this argument, we note that MWCNT are representative of porous materials with strongly attractive walls, where the magnitude of the interactions CCl_4 -carbon walls is high compared to the CCl_4 - CCl_4 interactions. For such systems we can expect an increase of the melting temperature in confinement, as compared to the bulk value.^{1,3} It is believed that the nature of the features observed in the C vs. T curves in DRS experiments depends on the amounts of bulk and confined fluid in the sample, since the signal is the sum of the two contributions. Therefore, we varied the amount of CCl_4 in the bulk phase and repeated the DRS experiments; we corroborated our previous results since the changes in the C vs. T curves were observed at essentially the same temperatures.

For the case of CCl_4 within open-tip MWCNT with an internal diameter $D = 2.8$ nm, in Fig. 3 we show experimental results for the capacitance C as a function of temperature T for a single value of frequency $\omega = 600$ kHz. Two jumps are observed at $T \sim 225$ K and $T \sim 250$ K, and a change of slope takes place at $T \sim 287$ K. As discussed previously, the first two transitions should correspond to the rhombohedral-monoclinic solid-solid transition, and to melting of bulk CCl_4 . Similarly, the transition taking place at 287 K may represent the point where all CCl_4 within the MWCNT is in liquid phase.

The results for melting of CCl_4 in MWCNT with internal diameters $D = 4.0$ and 2.8 nm present some differences with respect to results reported for CCl_4 within MWCNT with $D = 5.0$ nm.^{38,39} For this average internal diameter, we observed three phase transitions that could be related to melting of confined CCl_4 , at $T \sim 205$, 234 and 259 K;^{38,39} in addition, those transitions take place at temperatures below and above the bulk melting point of CCl_4 ($T = 250$ K). In contrast, in the present study, only one transition was associated with melting of confined CCl_4 in each case, $T \sim 272$ K ($D = 4.0$ nm, Fig. 2) and $T \sim 287$ K ($D = 2.8$ nm, Fig. 3); those temperatures are well above the melting point of bulk CCl_4 . Our finding of an increase in the confined melting temperature as the pore size is reduced, is consistent with results for fluids confined in slit-like, strongly attractive pores by Klein and Kumacheva,²⁸ and

Miyahara and coworkers;³⁶ both studies report that a reduction in pore size leads to a confined liquid to solid phase transition at temperatures well above the bulk freezing point. Our results also agree with previous molecular simulation studies^{40,43–46} of freezing of molecules confined in strongly attractive cylindrical pores with different diameters. The increase in the freezing temperature upon reduction of pore diameter was explained since the adsorbate-wall attractive interaction becomes stronger as the pore diameter is reduced, leading to larger increases in the solidification temperatures, at least for the molecular layers close to the pore walls.

Our DRS results for CCl_4 inside MWCNT with $D = 4.0$ nm and $D = 2.8$ nm are in qualitative agreement with our previous molecular simulation results for model CCl_4 within model MWCNT with similar diameters, $D = 3.9$ nm and $D = 2.8$ nm.⁴⁰ For both of these model systems, parallel tempering simulations in the grand canonical ensemble show that all regions of adsorbate experience a sharp change in their local degree of crystallinity simultaneously as T is varied.⁴⁰ This is consistent with what was observed in our DRS experiments, where only one transition was observed for confined CCl_4 for both pore diameters. The simulations suggest that the melting process takes place in the temperature range 270–282 K ($D = 3.9$ nm) and 295–318 K ($D = 2.8$ nm), a somewhat reduced temperature range when compared to that observed for CCl_4 freezing within a MWCNT of $D = 5.0$ nm (190–260 K).⁴⁰ In our DRS measurements, we note that the melting process upon confinement could have started at temperatures lower than $T \sim 272$ K ($D = 4.0$ nm) and $T \sim 287$ K ($D = 2.8$ nm), since the C vs. T curves exhibit changes of slope at temperatures lower than those (starting at $T \sim 265$ K for $D = 4.0$ nm, Fig. 2, and $T \sim 281$ K for $D = 2.8$ nm, Fig. 3). Our previous DRS results for CCl_4 within MWCNT with $D = 5.0$ nm suggest that melting upon confinement takes place in the temperature range 205–259 K.^{38,39} The simulations overestimate the range of temperatures in which melting upon confinement occurs, with the discrepancy becoming larger as the pore diameter is reduced. This suggests that the adsorbate-wall potential used in our previous simulations⁴⁰ is an accurate representation of the real adsorbate-wall interaction for the case of $D = 5.0$ nm, but becomes somewhat too attractive for smaller pore diameters since the adsorbate-wall attractive interaction becomes stronger as the pore diameter is reduced.

Conclusions

We have presented dielectric relaxation spectroscopy measurements of the melting point of carbon tetrachloride within open-tip multi-walled carbon nanotubes with two different pore diameters, 4.0 and 2.8 nm. In both cases, we have observed one transition corresponding to melting of the confined adsorbate, at temperatures well above the bulk freezing point of CCl_4 ($T \sim 272$ K for $D = 4.0$ nm, and $T \sim 287$ K for $D = 2.8$ nm). These results contrast with our previous DRS measurements for carbon nanotubes with a pore diameter of 5.0 nm,^{38,39} where multiple transition temperatures both above and below the bulk melting point of CCl_4 were observed. Our results show that the melting temperatures of CCl_4 confined in MWCNT increase as the pore diameter decreases, in contrast to what was observed for adsorbates confined within weakly attractive, siliceous cylindrical pores. These results are in agreement with previous experimental studies in strongly attractive slit pores where the pore width was varied.^{28,36} Our DRS measurements also agree with molecular simulation results of freezing of fluids within strongly attractive cylindrical pores.^{40,43–46} We compared our DRS measurements with our recent molecular simulation results for equivalent model systems.⁴⁰ The simulations overestimate the temperatures in which melting in confinement occurs, with the discrepancy becoming larger as the pore diameter is reduced, suggesting

that the potential adsorbate–wall used in the simulations⁴⁰ is somewhat too attractive for $D < 3.9$ nm. Nevertheless, the simulations show that all regions of adsorbate freeze simultaneously at the same temperature, and freezing occurs at higher temperatures upon reduction of the pore diameter, in qualitative agreement with our experimental results.

Further experiments with different techniques are needed to corroborate our observations. Differential scanning calorimetry experiments should corroborate the measured transition temperatures, while techniques such as X-ray diffraction and neutron scattering are suitable to determine the structure of the adsorbed phase. From the simulation viewpoint, our future work will focus not only on the effect of the adsorbate–wall interactions on freezing upon confinement, but also on how freezing of simple fluids within weakly attractive silica pores is affected by the pore surface roughness and morphological defects. We have studied how gas adsorption and capillary condensation is affected by these pore features,^{47–49} and we are currently assessing the effect on freezing in confinement.

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