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Heat of Fusion of Primary Alcohol Confined in Nanopores

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Heat of Fusion of Primary Alcohol Confined in Nanopores

By

Harrisonn Griffin

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Submitted in partial fulfillment
of the requirements for
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Abstract

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ADVISOR: Amanuel, Samuel

Melting behavior of physically confined 1-decanol in nano porous silica was probed using a Differential Scanning Calorimeter (DSC). In agreement with the Gibbs-Thomson prediction, we observe that the melting temperature of the confined 1-decanol scales inversely with the physical size of the pores. Contrary to the assumption used in developing the Gibbs-Thomson equation, however, the apparent heat of fusion decreases as the pore size decreases. Previously, several models have been proposed where interfacial layers of molecules do not participate in the phase transition and thereby would not contribute to the heat of fusion. While these could reconcile the seeming contradiction, annealing the nano confined materials enables some of the interfacial layers to be incorporated into an existing crystal. This leads to an increase in the apparent heat of fusion and a systematic relationship exists between the annealing temperature and the increase in the apparent heat of fusion.

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2 Introduction

When the physical size of a material is restricted to a few nanometers, its thermodynamic properties change from that same material in bulk scale. Typically, the melting temperature decreases as the size of the material decreases [1–4]. This is a result of an increase in surface to volume atoms. Surface atoms have fewer bonds, and therefore have less cohesive energy. Since cohesive energy is proportional to the melting temperature of a material, surface atoms will melt at lower temperatures than volume atoms [5]. The large number of surface atoms in nanomaterials means that nanomaterials will have lower melting temperatures.

The change in the melting phase transition temperature, called the melting point depression, is the transition temperature of the bulk material minus the nano material. The melting point depression scales linearly with the inverse size of the material. This relationship is explained by the Gibbs-Thomson equation,

$$\Delta T_m = T_m - T_m(r) = \frac{2\sigma_{ws}T_m}{\Delta H r}, \quad (2.1)$$

where ΔT_m is the melting point depression, T_m is the melting point of the temperature of the bulk material, r is the radius of the size of the material, σ_{ws} is the surface energy, and ΔH is the latent heat of fusion of the material. The Gibbs-Thomson equation assumes that the latent heat of fusion is constant, and therefore independent of size. However, experiments in which materials have been physically confined to nanopores [6] have revealed that the apparent heat of fusion for nano materials is smaller than that of bulk materials and varies based on the physical size of the material. This behavior has been observed in a variety of different materials including, but not limited to, cis-decalin, trans-decalin, cyclohexane, benzene [6].

The motivation for this study comes from observations of decreased heat of fusion in nano confined cyclohexane, 1-decanol, and 2-decanol [7,8]. The current explanation for the decrease in apparent heat of fusion is that it is being over normalized in calculations. In order to calculate the heat of fusion for a specific sample, we divide the entire phase transition energy by the mass of the sample. This normalization assumes that all of the sample material is undergoing phase transition. However, studies have shown that there exists a layer of surface molecules at the boundary of the pore that do not partake in phase transitions [7] and therefore do not contribute to the transition energy of the material. Since the heat of fusion is determined using the entire sample mass, not just the mass of the material undergoing phase transition, we say it is being over normalized. If we were able to force molecules in the surface layer to participate in the phase transition, we would be able to increase the mass of participating material, thus increasing the apparent heat of fusion.

One way in which we might be able to incorporate the interfacial layer is through the process of annealing. Annealing a sample at a partial melting temperature forms crystal seeds inside of the material. These crystal seeds ultimately encourage the sample to undergo a rapid and uniform crystallization, encouraging the surface layer of molecules to participate in the phase transition [1]. Previous experiments have revealed that annealing samples of 2-decanol at various times and temperatures can increase the apparent heat of fusion of by as much as 25% [9,10]. Although 2-decanol shows that the apparent heat of fusion can be increased through annealing, we cannot conclude that this behavior exists for other materials.

Observations of an increase in heat of fusion from annealing 2-decanol gives merit to the interfacial layer model, but it doesn't definitively prove that this is what occurs in material confinement. Therefore, the natural progression for our experiment is to see if this behavior exists in other materials. We chose to study

1-decanol confined in nanoporous silica dioxide. We annealed samples at various temperatures and looked at the effects of annealing on the heat of fusion.

3 Experimental

In order to study materials at the nanoscale, we need to be able to physically constrain materials to the nanoscale. A simple way to limit the size of a material is to put it inside of nanopores. The material being restricted inside the pores is known as the guest material and the containing pores are known as the host material.

The primary alcohol chosen as the guest material for this study was 1-Decanol, obtained from Sigma-Aldrich Chemical Company. In bulk, 1-Decanol has a melting point of 6.3°C and is a clear colorless liquid at room temperature. 1-Decanol, $C_{10}H_{21}OH$, is a non-chiral straight chain fatty alcohol. It is composed of ten carbon atoms with a hydroxide ion on the first carbon atom. It is primarily used in the production of lubricants and surfactants and is being investigated in the use of transdermal drug delivery.

The host material for the study was a mesoporous silica powder obtained from Sorbent Technologies. The silica powder consisted of SiO_2 particles ranging in diameter from 40-75 μm , with each particle containing a network of pores of a specified diameter running through its entire volume. We used four different silica powder samples with average pore diameters of 100, 150, and 200 Å. The silica powders' pore sizes have been reported as the average pore radius throughout a particle. This means that there is a distribution of pore sizes, not simply one discrete size. However, the manufacturer did not provide any specific information on the pore distribution. To try and better characterize the silica, we performed Nitrogen adsorption on various pore sizes and analyzed it using BET analysis. For each sample tested, we concluded that there was a single distribution of pores. The distribution had a peak centered on the reported pore size and a width of approximately 30 Å.

For our experimentation, we filled the mesoporous silica powder with excess

1-Decanol. Excess 1-decanol means that there was a greater volume of 1-decanol than total volume of all of the pores. We consider any 1-decanol that is inside of a pore to be “confined” material and any outside of a pore to be “bulk” material. In earlier experiments, it was shown that samples could easily be contaminated with impurities during sample preparation in the open air; most likely due to vapor and moisture [8]. To prevent the chance of contamination, we performed sample preparation under vacuum.

Each sample was prepared using the same apparatus and methods. A sealed Erlenmeyer flask containing a small vial of silica powder was placed on top of a hot plate. The flask was connected to a liquid nitrogen trap via a rubber hose, with another hose connecting the nitrogen trap to the vacuum pump. The hose connecting the flask to the nitrogen trap has two valves which were used to control and regulate the vacuum of our sample, allowing us to seal the samples separately from the nitrogen trap. The apparatus is shown in Figure 1.

The silica powder was first heated on the hot plate at 150°C for 20 minutes while under vacuum. Emitted vapors from the silica were removed from the flask via vacuum and condensed inside the nitrogen trap, thus eliminating the possibility of being reintroduced to the sample. The samples, now free of moisture, were left to cool to room temperature while still under vacuum. We introduced approximately 2 mL of 1-decanol into our system by injecting a filled syringe into the flask. The sample was left under vacuum in order to allow the 1-decanol to diffuse and fill all of the pores of the silica. Finished samples were stored in a refrigerator in order to prevent sample loss through evaporation.

To prepare a sample to run in the DSC, confined and bulk 1-decanol was put into a small aluminum pan. Some of the excess bulk was removed by dabbing the sample with a piece of filter paper repeatedly. The pan was hermetically sealed by crimping an aluminum lid to the top with the purpose of preventing evaporation.

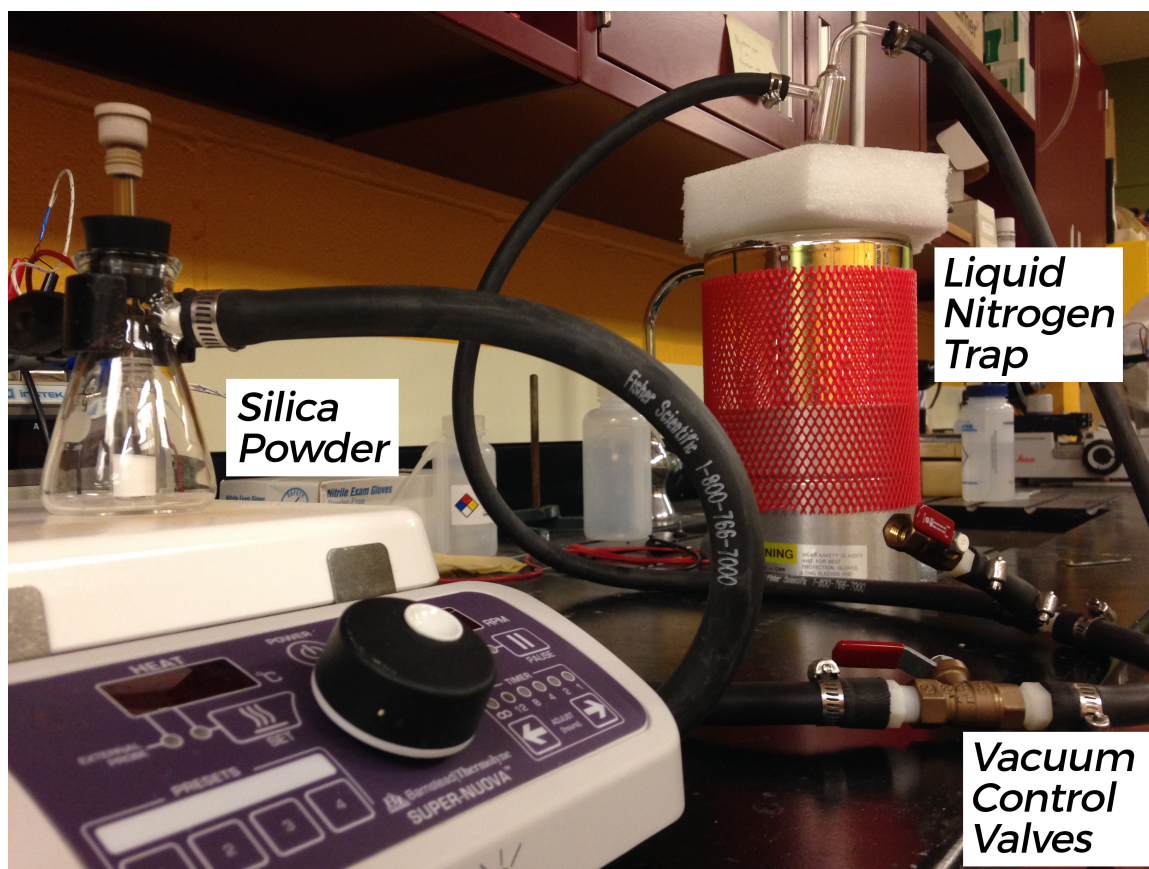


Figure 1: The set up for preparing samples of nonconfined 1-decanol. The flask on the heat plate, containing a vial of silica powder, is attached to a liquid nitrogen trap via a hose with valves to control the vacuum of the sample. 1-decanol is injected to the silica powder via needle through the rubber nozzle on the flask.

The sample can then be placed in the DSC and heated and cooled to various temperatures. The DSC measures the amount of heat required to change a sample's temperature as a function of temperature. The energy required for the phase transition can be found by simply integrating the area under phase transition curves.

4 Results

In this experiment, we used a DSC to study the melting of annealed and non-annealed nanoconfined 1-decanol. The three samples that we will be focusing on in this analysis are 1-decanol confined in 100, 150, and 200 Å pores. The primary focus was to study the effects of annealing on the behavior of confined 1-decanol, specifically on the energy required for melting samples.

In order to analyze the behavior of confined 1-decanol, we first need to understand its bulk characteristics. The DSC trace of melting and freezing of bulk 1-decanol is shown in Figure 2. The top curve is the endothermic melting peak, with the onset melting temperature at approximately 3°C. Note that there is a small shoulder peak on the left side of the bulk melting peak, which we believe to be a result of the rotator phase of 1-decanol. The lower curve is the exothermic freezing peak, with the onset freezing temperature at approximately 2.5°C. The small shoulder peak also appears on the left of the freezing peak, although it is not as noticeable. There is a small hysteresis of about 0.5°C between bulk melting and freezing peaks.

When we run a sample that contains both confined and bulk 1-decanol, we see that there are three melting peaks, as shown in 3. The rightmost peak corresponds to the bulk 1-decanol and the left two peaks correspond to the confined 1-decanol. We are able to take measurements of the onset temperature of melting and area under the curve for all of the melting peaks using the peak fitting program Pyris. Since all of the peaks have a width, mainly due to the distribution of particle sizes, we chose to use the onset of melting temperature as our measure of melting temperature. The onset melting temperature for each pore radius was calculated by averaging measured onset temperatures from several runs. The melting point suppression, ΔT , was calculated by subtracting these calculated onset melting temperatures from the average measured bulk melting temperature. We then plotted the

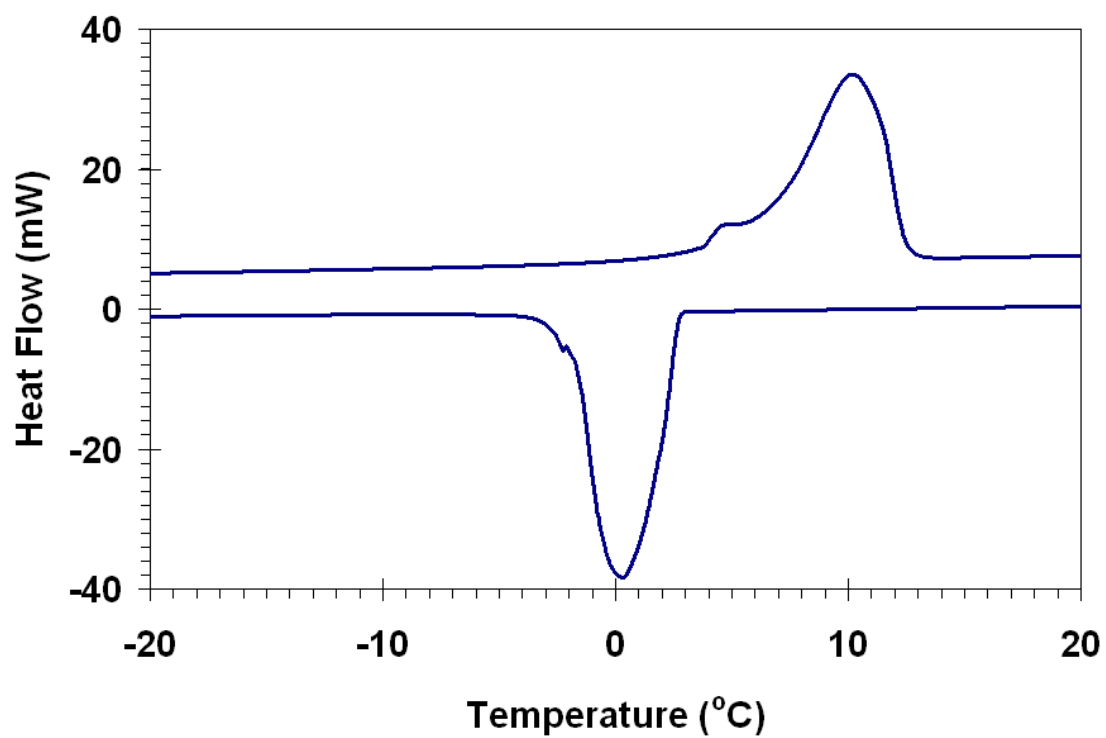


Figure 2: Heat flow as a function of temperature for bulk 1-decanol. Both the melting and freezing peaks have a characteristic shoulder to the left of the large bulk peaks. There is about a 0.5°C hysteresis between the melting and the freezing temperature.

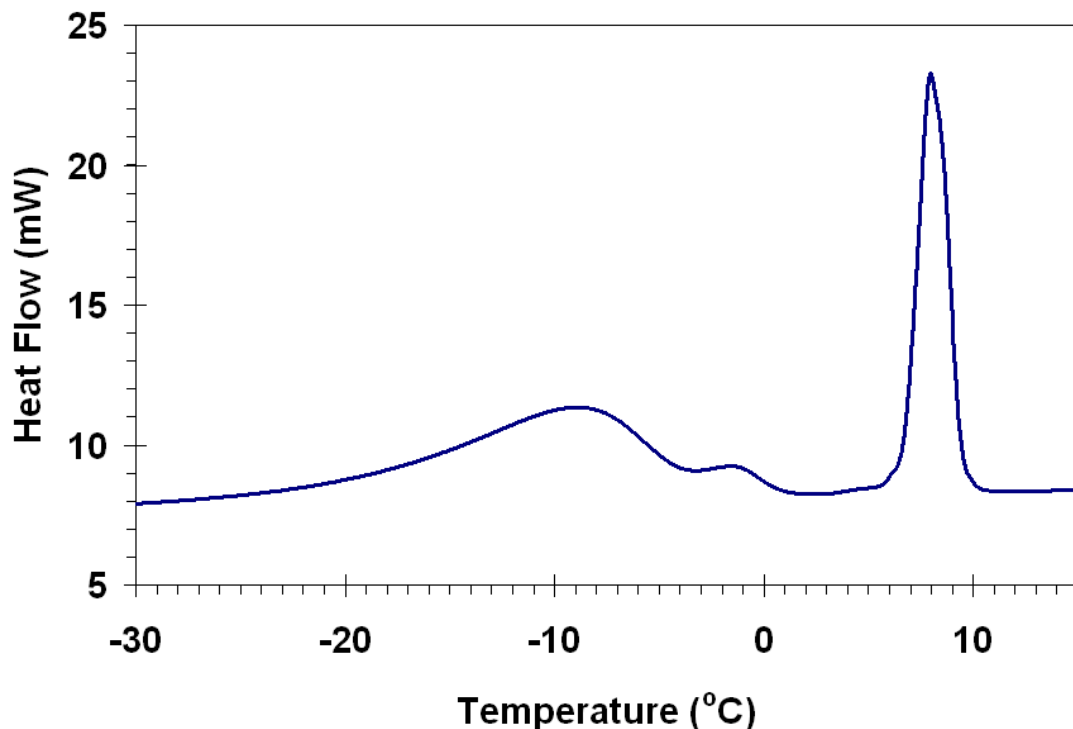


Figure 3: Heat flow as a function of temperature for bulk and confined 1-decanol. The bulk peak on the right still has the small shoulder present on the left. The left two peaks each represent confined material.

melting point suppression versus inverse pore radius, as shown in Figure 4.

When comparing these results to data collected in 2012 [8], we see that they both exhibit linear relationships but have different slopes and intercepts. Each result agrees with the Gibbs-Thomson equation, which says that there should be a linear relationship between melting point suppression and inverse pore radius. It is important to note that the silica nanopores used for each experiment were not identical. When comparing the differing slopes to the Gibbs-Thomson equation, we can say that the surface energy σ_{ws} must be different for the two host materials.

We then plotted melting point suppression versus inverse pore radius for annealed and non-annealed samples, as shown in Figure 5. The melting point suppression values are approximately the same for annealed and non-annealed samples. Again, this is in agreement with the Gibbs-Thomson equation. The linearity

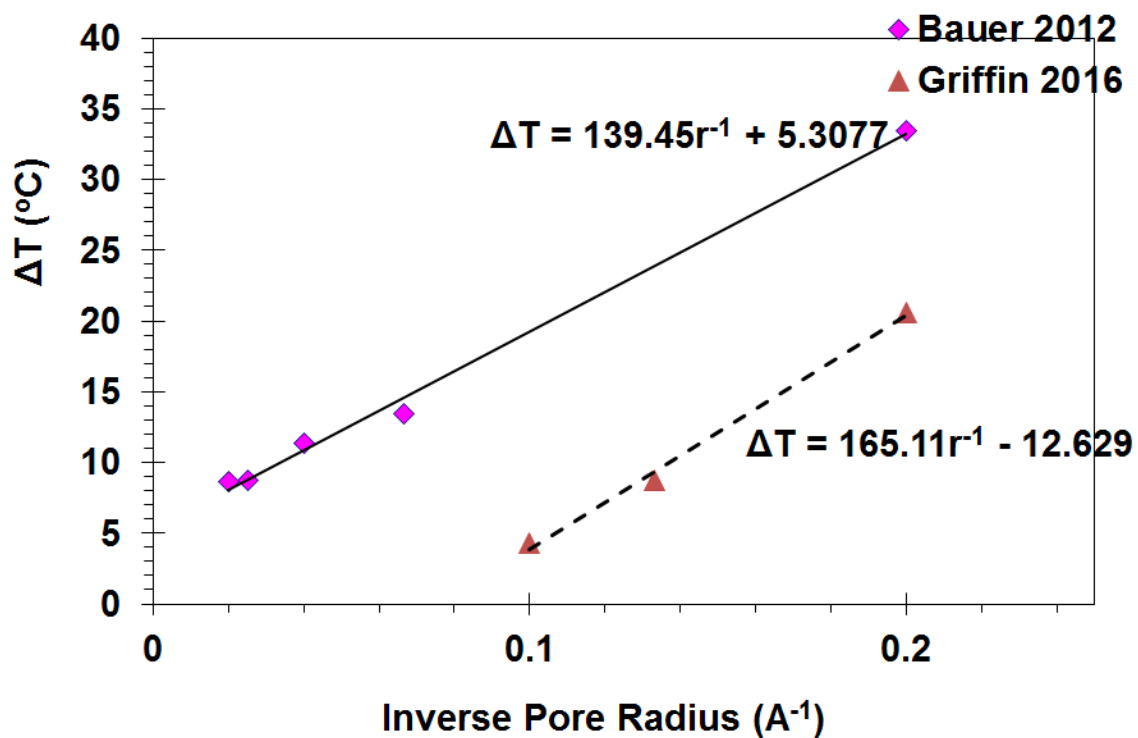


Figure 4: Melting point suppression ΔT as a function of inverse pore radius r^{-1} . The solid line data series corresponds to data collected in 2012 and the dashed line data series corresponds to data collected for this experiment. Notice that there is a linear trend for the two data sets, but the slopes and intercepts differ. The host materials are different, although they each report the same average pore sizes.

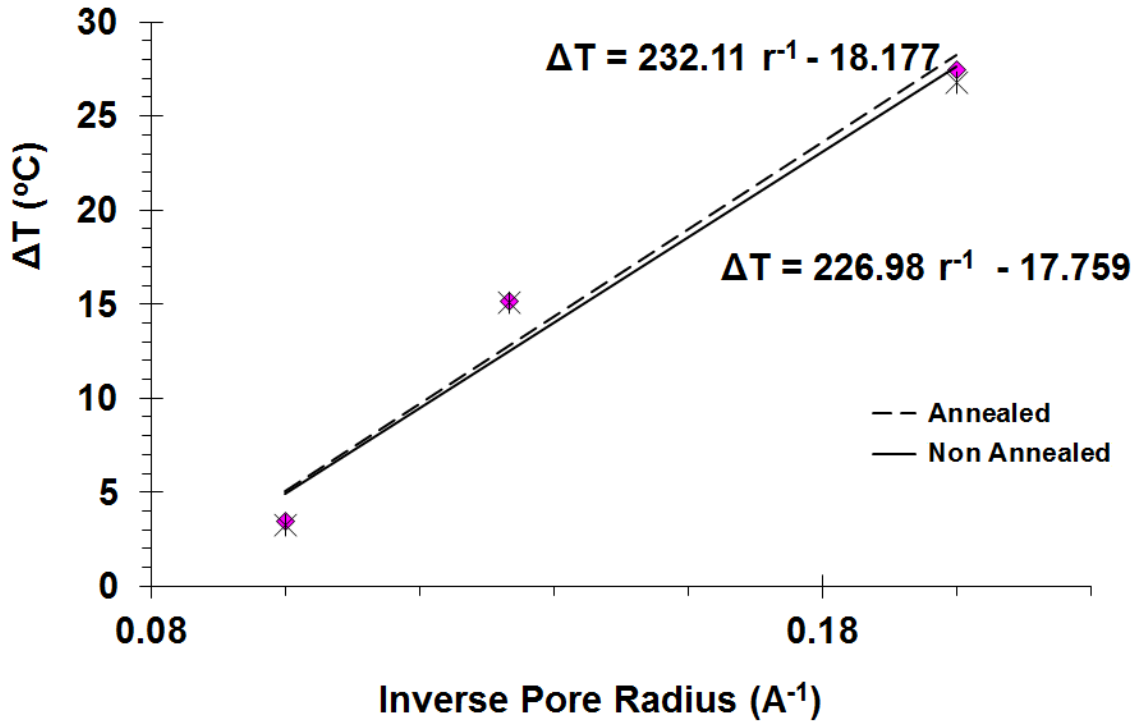


Figure 5: Melting point suppression ΔT as a function of inverse pore radius r^{-1} . The dashed line and pink diamond data series corresponds to melting point suppression of annealed samples and the solid line and crosses data series corresponds to melting point suppression of non-annealed samples. There is no significant difference between annealed and non-annealed samples.

of melting point suppression versus inverse pore radius found in both annealed and non-annealed samples implies that the heat of fusion ΔH is constant.

By annealing our samples at different temperatures, we found that there was a noticeable difference in the size of both of the confined peaks and the bulk peak, as shown in Figure 6. From a simply qualitative point of view, we can see that there are clear changes in the relative sizes of the peaks. Using A, the non-annealed sample, as reference, we see that B is smaller in the first confined peak, larger in the second confined peak, and has a taller bulk peak. Comparing C to A, we see that C has a larger first confined peak, a smaller second confined peak, and a smaller bulk peak.

The peaks seem to be coupled, that is as one confined peak increased in size the

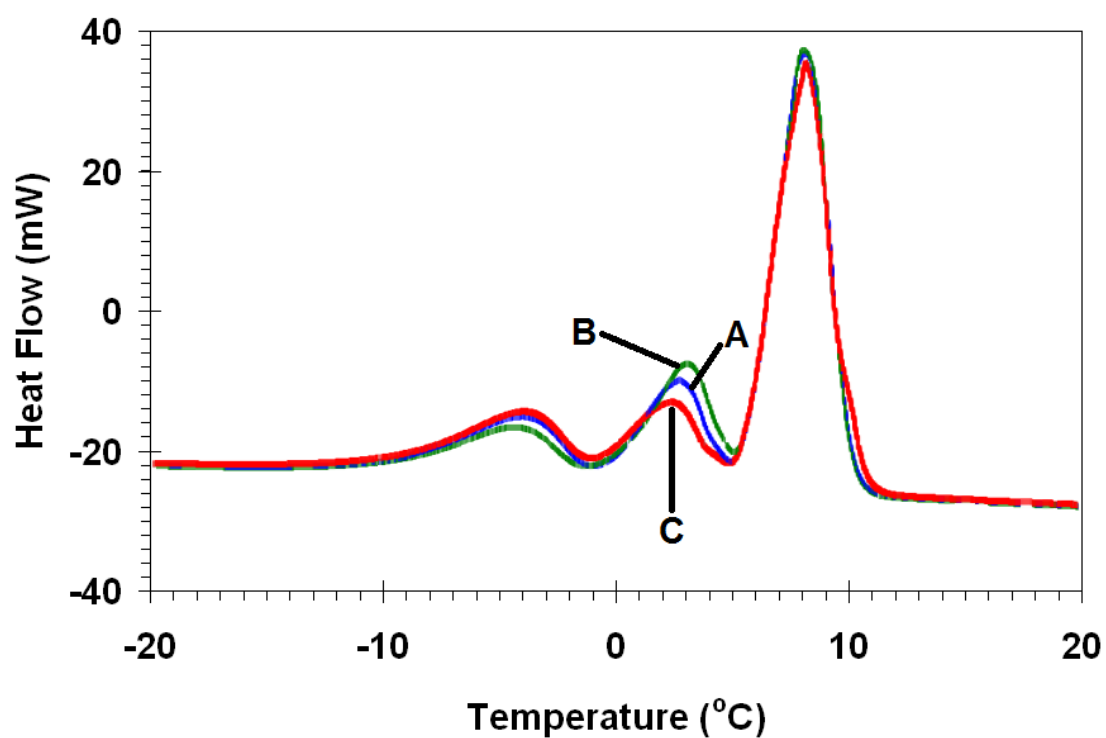


Figure 6: Heat flow as a function of temperature of 1-Decanol confined in 150 Å pores with bulk at three annealing temperatures. These annealing temperatures showed the greatest increase and decrease in confined peak size. A is non- annealed, B is annealed at 0°C and C is annealed at -10°C. B and C showed the greatest decrease and increase in area under the first confined peak, respectively.

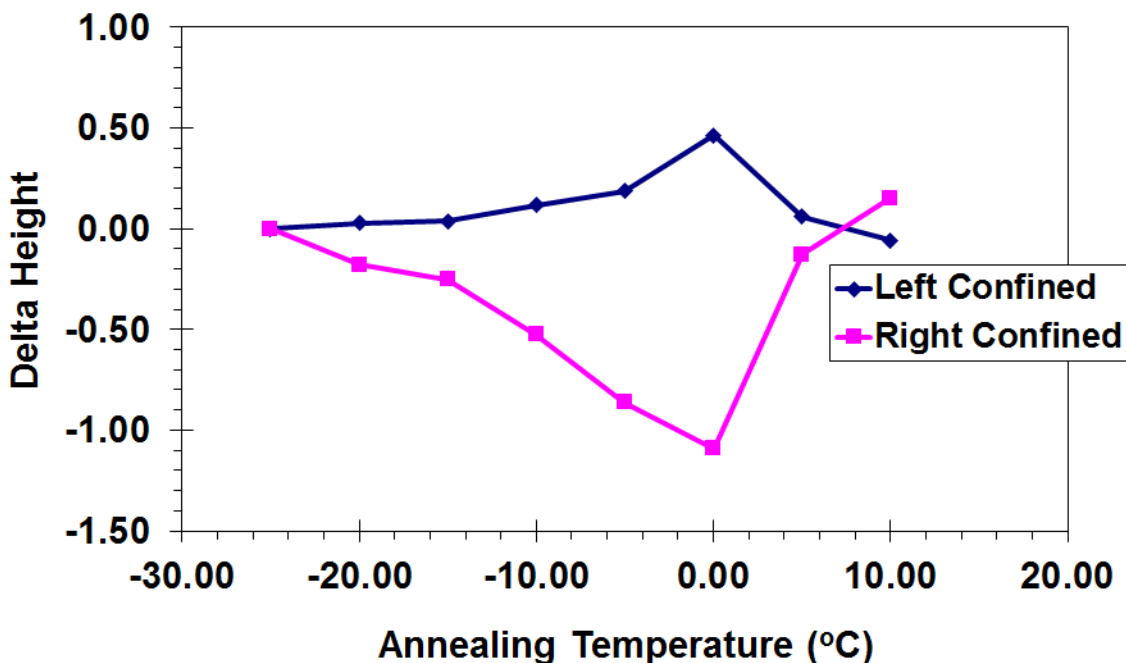


Figure 7: Relative heights of the two confined melting peaks as a function of annealing temperature for a sample with $R_p = 7.5\text{nm}$. We see that as one confined peak increases, the other will decrease, mirroring each other at each annealing temperature.

other would decrease. We plotted the relative heights of each peak versus annealing temperature, as shown in Figures 7 and 8. The 150 and 200 Å confined samples show similar behavior. As annealing temperature increases, the left confined peak increases until its maximum height at 0°C, and then decreases. The right confined peak decreases until its minimum height at 0°C, and then increases after.

To further understand the effect of annealing on our 100, 150, and 200 Å samples, we looked at and compared the areas of the leftmost confined peak. The areas were normalized against the non-annealed run such that we obtained a percent change in the area, which directly correlates to the change in the apparent heat of fusion ΔH . The percent change in area as a function of annealing temperature is shown in Figure 9. First looking at the 100 Å sample, we see that as the

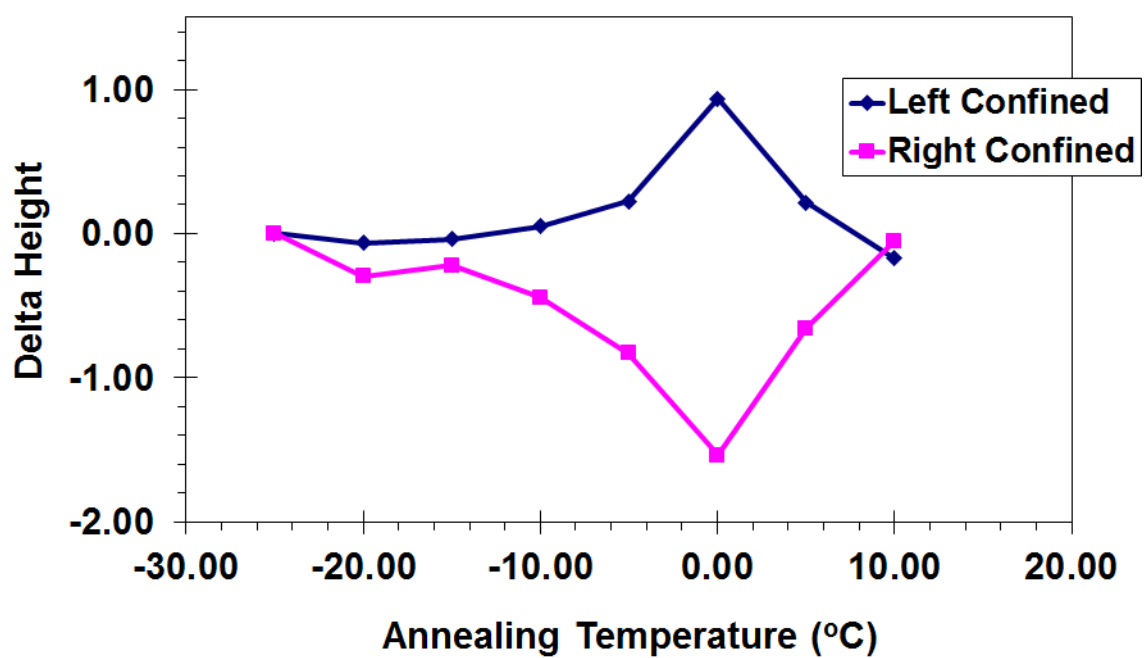


Figure 8: Relative heights of the two confined melting peaks as a function of annealing temperature for a sample with $R_p = 10\text{nm}$. Just like Figure 7, we see that as one confined peak increases, the other will decrease, mirroring each other at each annealing temperature.

	Maximum Increase		Maximum Decrease	
	% Change	Annealing Temp (°C)	% Change	Annealing Temp (°C)
Rp=5nm	10.20	0	-16.19	-10
Rp=7.5nm	9.59	-10	-16.69	0
Rp=10nm	1.85	-16	-19.69	0

Table 1: The maximum increases and decreases in percent change of area of the left confined peak and their corresponding annealing temperatures for the data presented in Figure 9.

annealing temperature increases the percent change begins to decrease. It continues to decrease until the percent change reaches a minimum of -16.19% at -10°C. As the annealing temperature continues to increase, the percent change increases until a maximum increase of 10.20% is reached at 0°C. As annealing temperature increases, the percent change falls back towards 0%.

The 150 and 200 Å samples behave in the same way as each other, but are dissimilar from the behavior of the 100 Å sample. As the annealing temperature increases, the 150 and 200 Å samples initially experience a small dip at -20°C, but then increase until they both reach a maximum increase at -10°C. The 150 Å reaches a max increase of 9.59% and the 200 Å sample 1.85%. As annealing temperature increases, the percent change then decreases until the 150 and 200 Å hit a minimum of -16.69% and -19.69%, respectively. Then both samples increase again towards 0%. It is interesting to note that the 100 Å sample appears to mirror the 150 and 200 Å samples. That is, if we were to reflect the 100 Å across the x axis, all three samples would have nearly identical behaviors. The changing size of the peaks as a result of annealing implies that each melting phase is requiring a different amount of energy. This suggests that annealing our samples at various temperatures influences the crystallization of 1-decanol.

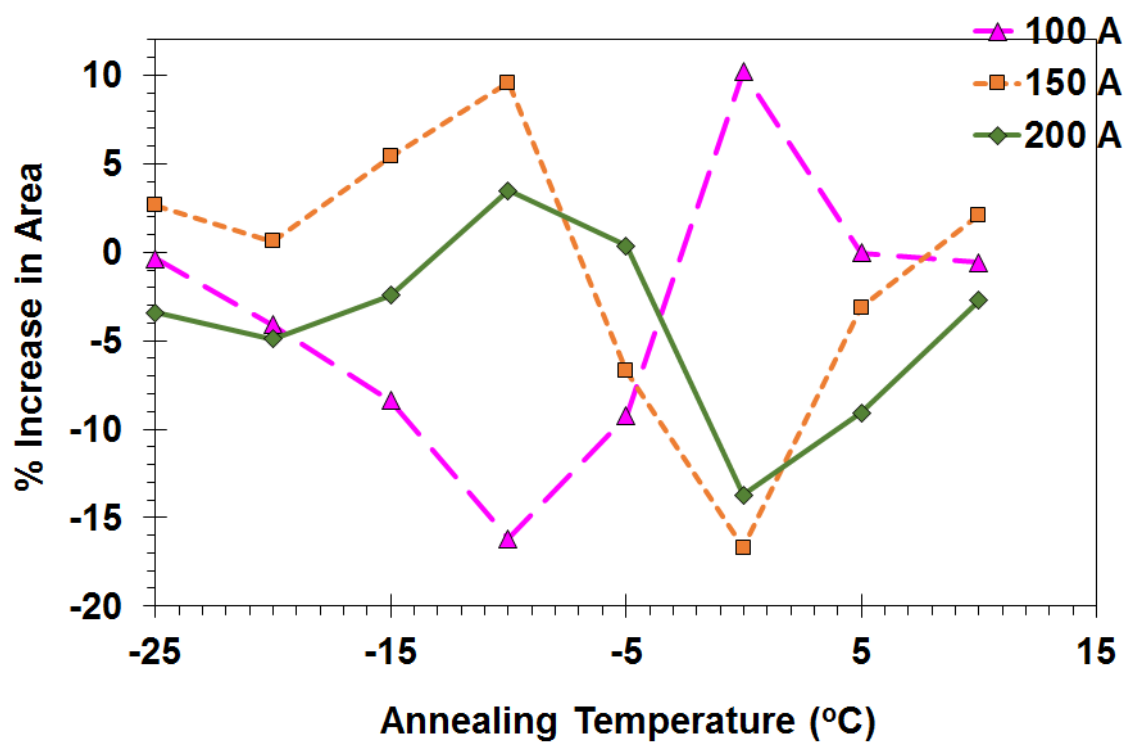


Figure 9: The percent change in area for the leftmost peak of melting confined 1-decanol as a function of annealing temperature for pores of radius 5, 7.5, and 10 nm.

5 Conclusion

In this experiment we studied nanoconfined 1-decanol and the effects of confinement on its melting properties. We specifically annealed 1-decanol confined in silica nanopores at various temperatures to induce partial melting, cooled the samples back down to freezing temperatures, and then fully melted the crystals.

The onset melting temperature for confined 1-decanol acts in agreement with the Gibbs-Thomson equation, as suggested by the linearity of Figure 4. That is, as confining pore size decreases, the onset melting temperature decreases. When the confined 1-decanol is subjected to annealing, we see very little change in the onset melting temperature, as seen in the fits in Figure 5. Although the onset remains unchanged, we see variation in the size of the confined peaks, as shown in Figure 6. The first and second confined peak appear to mirror each other; when one peak increases the other will decrease, as shown in Figures 7 and 8.

Looking at the leftmost confined peak, we see that different annealing temperatures can cause the area of the peak to increase and decrease. Figure 9 shows the relative changes of the apparent heat of fusion as a function of temperature. All three pore sizes have a maximum and minimum, showing percent changes as large as 20%. Since there is no recorded mass loss of our samples greater than 0.02 mg, we know that this change cannot be attributed to the mass of the 1-decanol. However, the dynamics of the crystallization of 1-decanol within a pore can explain this behavior. At near melting annealing temperatures, there are two competing mechanisms; the melting of 1-decanol confined in smaller pores and annealing of 1-decanol in larger pores.

There is a balance between growth kinetics and melting, with crystal seeds formation being more frequent at lower temperatures and melting dominating at higher temperatures. This means that different annealing temperatures can promote the formation of different crystal structures. Additionally, the relative chang-

ing sizes of the confined peaks suggest that there is crosstalk between 1-decanol confined in different pore size regimes. For example, a larger leftmost confined peak and smaller right confined peak might suggest that more 1-decanol is moving from larger pores to smaller pores. More mass in the smaller pores would cause an apparent increase in the heat of fusion.

An alternative explanation for the mechanism of annealing is that the 1-decanol experiences polymorphism when confined in nanopores. Polymorphism gives materials the ability to crystallize in different structures as a result of competition between nanometer-scale molecule clusters. This behavior reveals that the stability of thermodynamic properties of embedded phases are directly linked with nucleation at these confining length scales. Studies have shown that polymorphism can be controlled via confined crystallization at the nanoscale [11, 12]. Since confinement can provoke the formation of polymorphs and annealing can plant various crystal seeds inside of partially melted 1-decanol, we suggest that different annealing conditions promote the formation of different polymorphs.

Heating confined 1-decanol at near melting temperatures causes melting of 1-decanol in smaller pores and annealing of 1-decanol in larger pores. In order to see if there is crosstalk between the bulk and the two confined peaks, we need to study the effects of annealing samples that contain only confined 1-decanol. Previous experiments have shown that it is possible to evaporate off excess bulk from samples. In doing so, we will gain a better understanding of what material the two confined peaks actually represent, and to what extent the bulk affects their behavior. Additionally, to see if nanoconfined 1-decanol exhibits polymorphism, we need to perform XRD measurements on various annealed samples and study their crystal structures.

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