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Annealing 2-Decanol in Nano-confined Systems:
Effects of Annealing Time

By
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of the requirements for
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Abstract:

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Annealing 2-Decanol in Nano-confined Systems: Effects of Annealing Time

Department of Physics, June 2015

Advisor: Samuel Amanuel

We studied melting and freezing of 2-decanol nano-crystals (100 Angstrom to 1000 Angstrom) using a Differential Scanning Calorimeter (DSC). In agreement with the Gibbs-Thompson equation, the melting temperature of nano crystals decreases with physical size and its change scales linearly with the inverse of physical size. The apparent heat of fusion of the nano scaled systems, however, has been found to be lower than the heat of fusion for the bulk. Although this is in agreement with previous experimental observations, it is in contradiction with the assumptions used to develop the Gibbs-Thompson equation. We believe that the apparent heat of fusion needs a correction since material at an interface may not crystallize under typical freezing conditions. We are able to demonstrate that we can increase the apparent heat of fusion by as much as 23% by annealing the nano scaled systems and that the heat of fusion increases with annealing time while the suppression of melting temperature due to confinement decreases with annealing time.

Introduction:

Confining a material that crystallizes on the nano-scale leads to some novel behavior. Specifically, confining a crystallizing material lowers its melting temperature. Crystallization behavior in nano-scale systems has been studied before and is thought to be governed by the Gibbs-Thompson equation shown in the equation below.

$$\Delta T_m = T_m - T_m(r) = \frac{2\sigma_{ws}T_m}{\Delta H r} \quad (1)$$

Where ΔT_m represents the change in melting point, T_m is the melting point of the material, σ_{ws} is the surface energy, r is the pore radius and ΔH represents the heat of fusion for the material. According to the Gibbs-Thompson equation, this lowering of temperature should be proportional to inverse pore size as it should change in relation to $1/r$. In previous experiments¹ this has observed that this relation holds for 2-Decanol confined in silica nanopores.

It has been suggested that the 2-Decanol adjacent to the pore walls does not fully take part in the freezing process and therefore the full body of the confined decanol does not participate in the thermal process of melting². However, when the sample is annealed, we can force some of this non-freezing layer into participation in the crystallization process and therefore when we melt the sample we see a higher latent heat of fusion as we are attempting to melt more material. Specifically, we believe that the annealing process, causing a partial melt, leaves crystal seeds within the material. Due to the presence of pre-existing crystal seeds, the crystallization process happens more rapidly and more uniformly. This therefore makes it easier for more of the material to participate in the process and therefore easier for

¹ Amanuel et al. (2009)

² Bauer (2012)

the outer layers to crystallize with the rest of the confined material. In previous experiments³ we have verified that annealing has the desired effect on confined material.

By annealing a sample we can change the measured melting temperature and measured latent heat of fusion so that it approaches that of the bulk material. Therefore the natural progression for our experiment would be to look at the effect of the annealing time itself on the process. Historically, we've looked at the annealing with a fixed time of one minute for resting at the annealing temperature. It is possible, given our hypothesis of increasing engagement, that staying on the isothermal for a longer period would increase engagement of these non-participating sections and that this could coerce an even higher latent heat of fusion.

Experimental Procedure:

We conducted this study using a 2-Decanol solution acquired from Aldrich Chemical Company. 2-Decanol is a molecule composed of ten carbon atoms in a chain with an OH group attached to the second carbon. It is particularly useful for our experiments as there is a significant hysteresis of the melting and freezing temperatures of 2-Decanol of about 20 degrees Celsius. The melting point of bulk 2-decanol is around -3°C

We also obtained porous silica beads from Sorbent Technologies. These beads contained small porous networks on the nanoscale. We used pore samples with sizes ranging from 100-1000 Angstrom. These sizes refer to the average size of the small network in the silica beads that give it its porous nature. For our purposes however, the silica system approximates small nanopores of those size. At the time of this experiment, we had prepared samples in which the beads were added to bulk 2-decanol and the bulk liquid was subsequently absorbed by the beads. The samples, separated by pore size, were then composed of confined 2-decanol within the beads as well as bulk 2-decanol outside the beads. These samples were then kept refrigerated to prevent sample loss due to evaporation.

We first prepared our experimental samples by taking a small amount of silica bead and bulk material and placing them in a small metal pan which we had weighed previously. The sample was then heated at 120°C for 3 minutes to remove as much of the bulk material as possible without affecting the 2-Decanol trapped within the silica beads. Once the bulk in the sample was evaporated, we then crimped a top on the metal pan to seal it and prevent further loss due to evaporation from the pores during the experiment. While 2-Decanol does have low vapor pressure and therefore tends to stay confined, this helped keep sample loss to an absolute minimum. The sealed sample was then reweighed and the previously known weight of the pan and lid were subtracted to obtain the weight of just the sample itself. We

used a Differential Scanning Calorimeter, abbreviated as DSC, to measure heat transfer to the sample during heating and cooling.

The sample was then placed in the DSC which was kept at 30°C. The sample was cooled from 30°C to -50°C to completely freeze the confined decanol. The sample was kept at -50°C for one minute. It was then heated back up to 30°C to obtain a characterization of the melting peak with no annealing process. This melting peak was used for comparison and normalization of the annealed peaks. We then again cooled the sample down to -50°C and kept there for one minute. The sample was heated to this middle temperature, the specific temperatures that samples were heated to depended on the pore size of the sample, and can be seen on their respective graphs in Figures 1 through 4, and kept there for one minute. The sample was then cooled to -50°C, held for one minute, and then heated back up to 30°C. This process was then repeated with the sample being held at the annealing temperature for different lengths of time. Specifically it was left for 10 seconds, 1 minute, 5 minutes, 10 minutes, 15 minutes, 25 minutes, and 30 minutes. The time periods the sample was annealed for were randomized in order. This process was completed for samples of pore size 100 Å, 300 Å, 500 Å, 800 Å, and 1000 Å. The samples were annealed at -6°C for all pore sizes except for the 1000 Å sample which was annealed at 1°C. These temperatures were chosen as they were in the middle of the melting range of confined decanol for samples of that pore size.

Results:

With our experiment, we used a Differential Scanning Calorimeter to study the effects of varying annealing time in 2-decanol that has been confined in silica nanopores. We found that increasing annealing time does increase the ΔH of the confined 2-decanol during the melting process but that this increase quickly levels off as can be seen in Figure 2. We also found that an increase in annealing time also shifts the melting peak of the confined 2-decanol higher. Both these effects are more noticeable when the sample has a small pore size.

We used the tools within the Pyris software to calculate the areas of the melting peaks that occurred during the heating process. We then normalized those areas to get a percentage change from the non-annealed condition of ΔH so as to get a data set that was comparable across different pore sizes. This normalization was achieved by dividing the area of the annealed peaks by the first non-annealed peak.

We looked at the effect that the annealing process had on the melting peaks themselves. The process itself is represented by the endothermic peaks that appear during the heating cycle of the 2-decanol. By visually comparing these peaks we can get a better sense of how the confined 2-decanol behaves once it is subjected to the annealing times and the effect on annealing for a longer period.

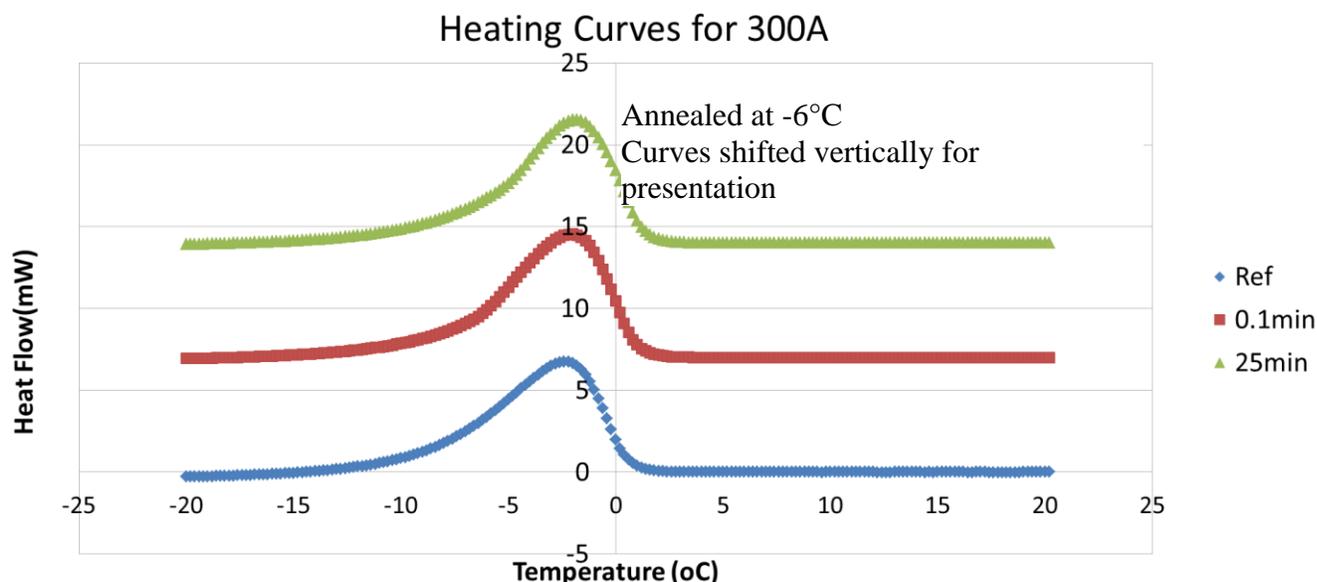


Figure 1: This is a set of heating curves for 2-decanol confined in 300 Angstrom Silica beads. The first curve was cooled to -50°C from 30°C and up to 30°C . The higher curves underwent the same process with the added step of being annealed at -6°C for 0.1 minutes and 25 minutes before being heated back up to 30°C . We can see an increase in peak size for the annealed peaks as well as a larger increase as annealing time increases which can be confirmed by measuring the area. We can also see a definite shift to the right of the peak as annealing time increases which is confirmed by looking at the onset of the peak and shown in Figure 4. Note that the higher peaks have been shifted vertically for ease of comparison.

This figure shows an example of the raw output data from the DSC for both annealed and non-annealed curves. Using the DSC software we can get the area under the curves to get the latent heat of fusion for the melting process. We can also check the onset of the peak to get a shift in the melting point due to confinement and annealing. This data is presented in Figures 2 through 4 shown below.

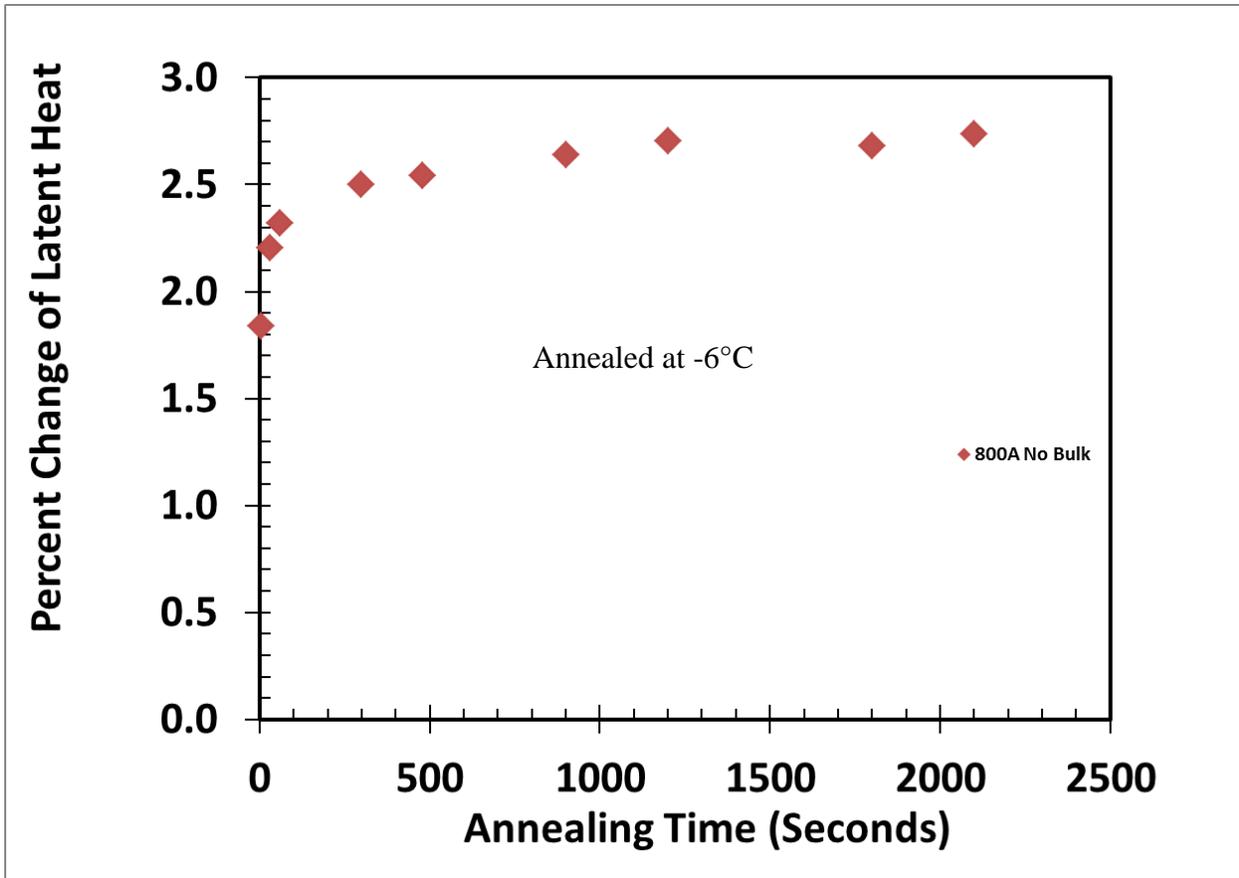


Figure 2: This Figure shows the effect of the amount of annealing time on ΔH . We can see from this that ΔH increases as a result of annealing time before reaching some terminal value at around a ten minute annealing time.

As we can see from Figure 2, when annealing time is increased, we see an increase in latent heat of fusion. This effect is increased up to a certain value at which point we see no greater level of increase. We can take the natural log of both axes and plot this data as can be seen in Figure 3 to show that this relationship is governed by a power law and therefore can be linearized.

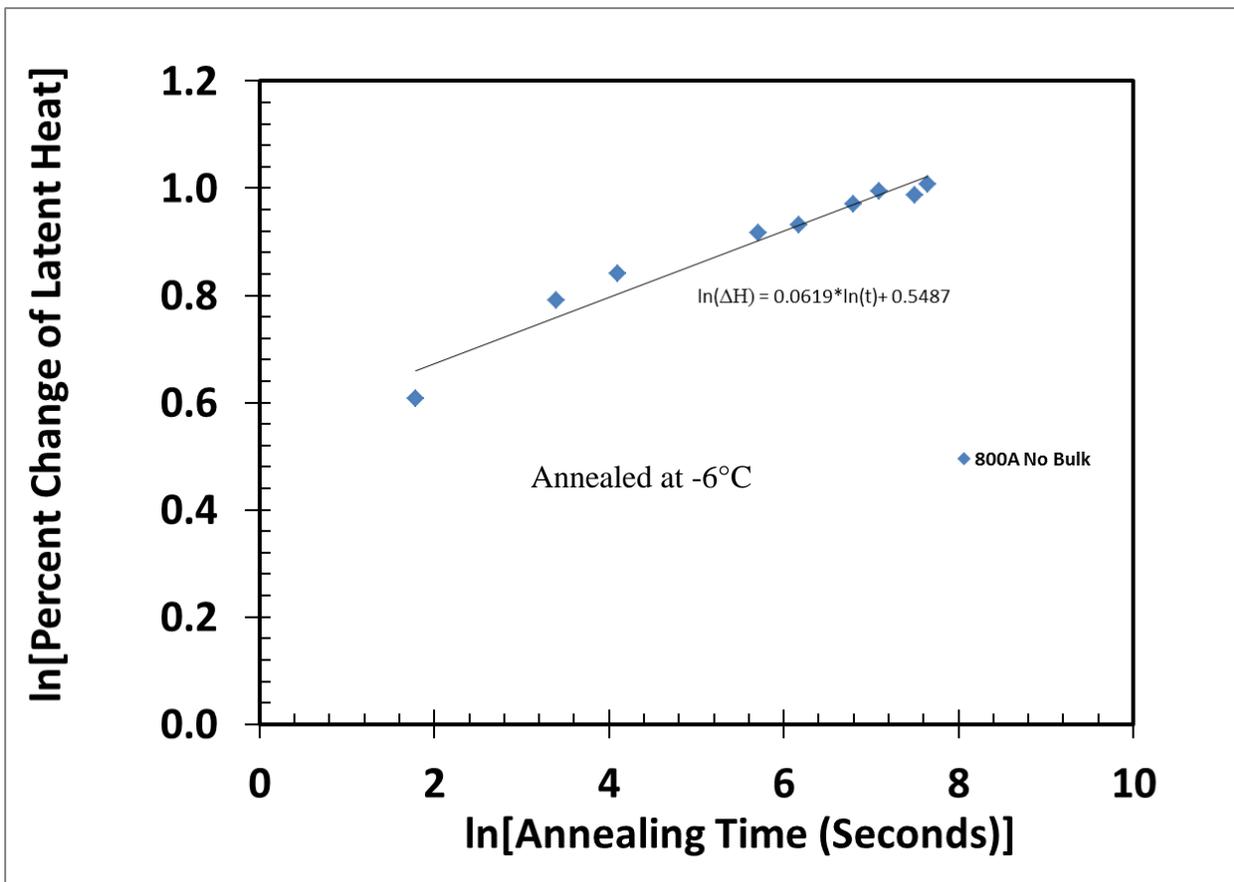


Figure 3: This figure shows the same data from Figure 2 plot but with the natural log taken of both annealing time and ΔH . The result is the linear relation between annealing time and ΔH , implying a power law relation between the two values.

Due to the linear relation shown in Figure 3, we can assume that there is a power law relation governing the relation between ΔH and annealing time. This challenges the assumption that ΔH is constant and lends credence to our theory that annealing is causing non-participating layers inside the nanopores to begin participating in the crystallization process.

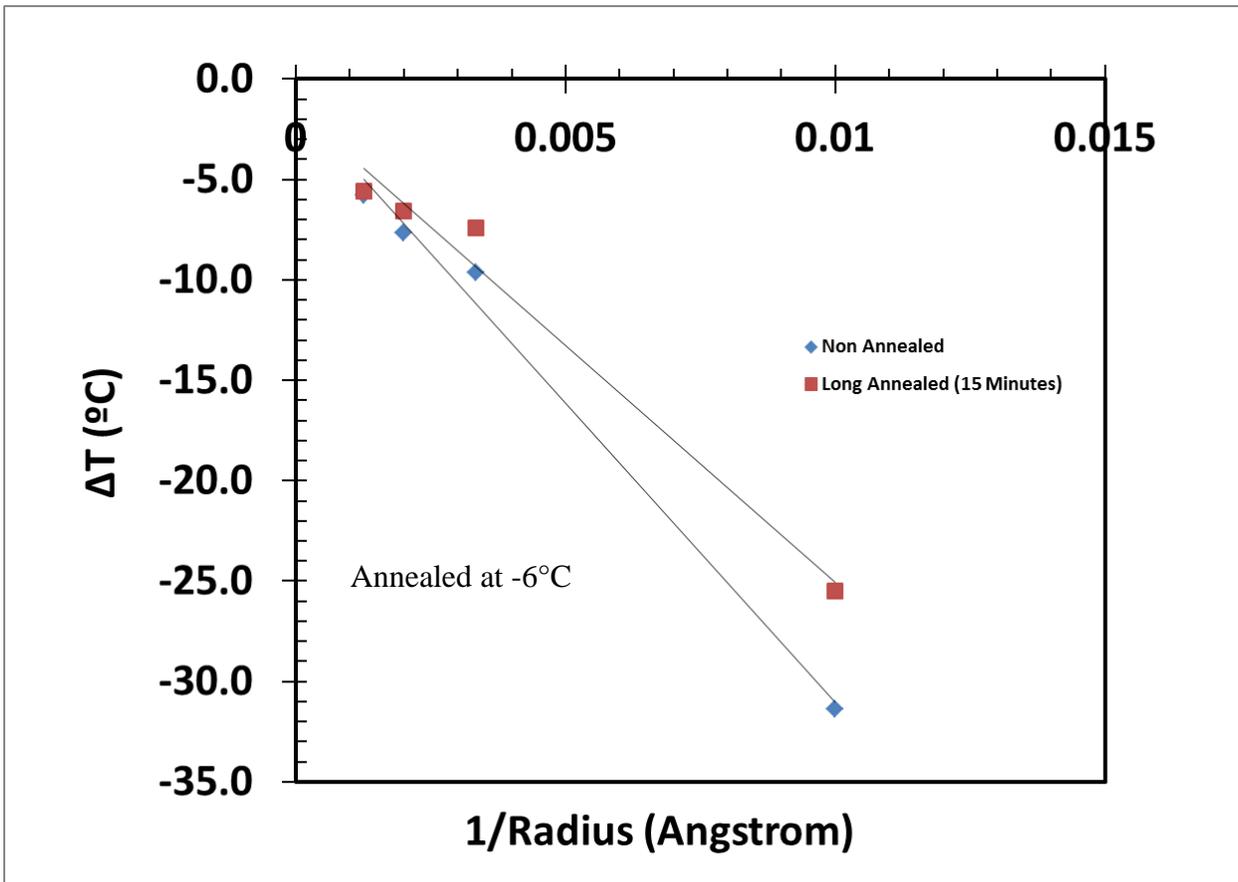


Figure 4: This figure shows the effect of annealing on the shift in melting temperature as a function of pore size. This relationship is governed by the Gibbs-Thompson equation and should be a linear function of $1/R$ where R is the radius. Here we see that the relationship continues to be linear in an annealed system but that the annealing process shifts that linear relation higher as the pore size gets smaller.

From Figure 4 we also see the effect of annealing on melting temperature. This tells us that, while the relationship is similar to the non-annealed condition under annealed conditions, the slope of the relationship is also dependent on the degree of the annealing and that this results in a smaller suppression of temperature at very small pores sizes.

Discussion and Conclusions:

We studied the melting peaks of confined 2-decanol in silica nanopores of varying pore sizes. These pore sizes are actually representative of the average size within a porous network in a silica sphere. Specifically, we annealed the 2-decanol at its melting temperature to partially melt it and then cooled it and melted it again. By doing this we were able to consistently induce an increase in the apparent latent heat of fusion for the 2-decanol as well as shift its melting peak to a higher temperature.

The most obvious effect of our experiment was the increase in the latent heat of fusion of the 2-decanol. We saw up to a 25% increase in the ΔH that depended heavily on the pore size of the material. At large pore sizes the difference could be as small as a few percent. We also found that keeping the sample at our annealing temperature for a longer period affected this change in ΔH . The latent heat of fusion would increase up through annealing times of a few minutes before quickly leveling out at some consistent value. This process too was much more apparent for small pore sizes over large ones.

We believe that this behavior is due to the dynamics of the melting and freezing process within the pore itself. 2-decanol undergoes a crystallization process. We believe that, if the pore is small enough, a significant layer of the 2-decanol material adjacent to the pore wall will not participate in the freezing process. Due to the way that the crystals form, a delicate balance is created between crystal seeds which form at lower temperatures and the propagation of the crystal front itself which is more likely at higher temperatures where the molecules still have relative freedom of movement. Due to the uneven nature of this formation, some liquid volume is left on the edge where there are more molecules that could not participate. By partially melting the structure, we believe that we melt part of the crystal without melting the crystal seeds themselves. These seeds act as nucleating agents which influence the refreezing process. Therefore, when we once again freeze the decanol we

induce a more even formation of the crystal and therefore minimize the material on the edge that does not participate. This therefore results in a higher latent heat of fusion as a greater amount of material is participating in the thermal process and therefore more energy is required to go through that process. This also explains why extending the process is only effective up to a point, as eventually the point is reached where no more of the crystal will melt at our annealing temperature and therefore continuing the melting process will not change our results.

Another important result from our experiment was the shift in the melting peak as a result of the annealing. Like the increase in ΔH , this behavior is only very apparent in samples with a small pore size. Specifically, it is most visible in pores of average size of 300 Angstrom or smaller. The behavior manifests itself on our graphs as a small shift of the entire system to the right. Also like the change in ΔH , this behavior is enhanced by an increased annealing time. The change is small, often only a few degrees, but is consistent to some extent across all samples.

We have observed this behavior before in previous experiments. Essentially, the annealing process itself naturally creates this shift, and in most cases a corresponding shift of the freezing peak up as well, though the shift of the freezing peak was not specifically looked at in this experiment. Since the confined 2-decanol itself melts and freezes at a temperature far below bulk 2-decanol, we can see this shift as another quality of confined 2-decanol being forced back towards bulk behavior. It also implies that the process itself has at least an induced heterogeneity as it appears that the presence of existing crystallization agents results in a crystallization that involves a greater amount of the confined material. While we cannot say for certain that the process is always heterogeneous, we can assume from this that it is not always homogeneous. The shift itself appears to be a result of both the increased amount of material that is being involved in the thermodynamic process as well as the specific

material. The smaller pore crystals will stay frozen leading to less behavior on the lower end of the temperature spectrum while the increased level of behavior on the edge of the pores makes the pore itself act as a larger space. That is, the volume of participating material is artificially made larger due to the increased edge participation and that could result in the shift that we are seeing.

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