Cryogenic Material Properties

The trunk of the tree of physics—explaining how things move—was established by Issac Newton ca. 1700. In the 1800s two new branches of physics were developed: thermodynamics and E & M (electricity and magnetism). Fundamental to thermodynamics is an understanding of temperature. Oddly enough while we can easily create arbitrary temperature scales, (for example, based on the thermal expansion of mercury between the freezing point and boiling point of water) temperature, T, has a most obscure definition:

$$\frac{1}{T} = \frac{\partial S}{\partial U} = k_B \frac{\partial \ln(\Omega)}{\partial U} \tag{1}$$

where S is entropy, U is the internal (thermal) energy, Ω is the number of microstates consistent with the macrostate and k_B is the Boltzmann constant (which basically established the size of the unit Kelvin).

Clearly something so abstruse cannot be a physicist's everyday working idea of temperature. Typically physicists think of temperature as proportional to the average random kinetic energy of the material: $T \propto U/N$ where N is the number of particles. One can immediately note some situations where this simplified notion fails. Clearly energy must be added to make material boil (the latent heat of vaporization) but the temperature does not change (the material remains at the boiling point temperature: T_{BP}). The simple view would account for this by noting that as liquid becomes gas the atoms are separated, which requires energy that we must supply. Additionally it is a theorem in thermodynamics that the specific heat of all materials must vanish as the temperature approaches absolute zero. But specific heat, c, is

$$c(T) = \frac{1}{m} \frac{\partial U}{\partial T} \tag{2}$$

which would be constant if $T \propto U/N$. Thus specific heats, which are typically tabulated at room temperature, are not constants but must get smaller at lower temperatures.

Thermodynamics can be formalized into something resembling Euclidean geometry with four 'Laws of Thermodynamics'. In that context the key theoretical quantity 'entropy' was discovered; it could be experimentally tabulated but had no known corresponding physical reality. In 1877 Boltzmann found the connection between the mechanics of particles and thermodynamics: $S = k_B \ln(\Omega)$ and felt that it so significant that it heads his tombstone. With the connection between thermodynamics and mechanics established it became possible to calculate thermal properties based on the motion of atoms[1]. (And also the reverse: to discover the nature of atoms by measuring thermal properties of bulk materials.) However if these atoms behaved as Newton discovered ('classically') contradictions with experiment were immediately obvious. Surprisingly the solution to these problems was to apply non-Newtonian laws of motion: quantum mechanics in the early 1900s.

---

[1]It is perhaps worth noting that the idea that material consists of innumerable small particles was not widely believed until ca. 1900, and that thermodynamics was singularly significant in 'proving' atoms actual existence via successful theories.
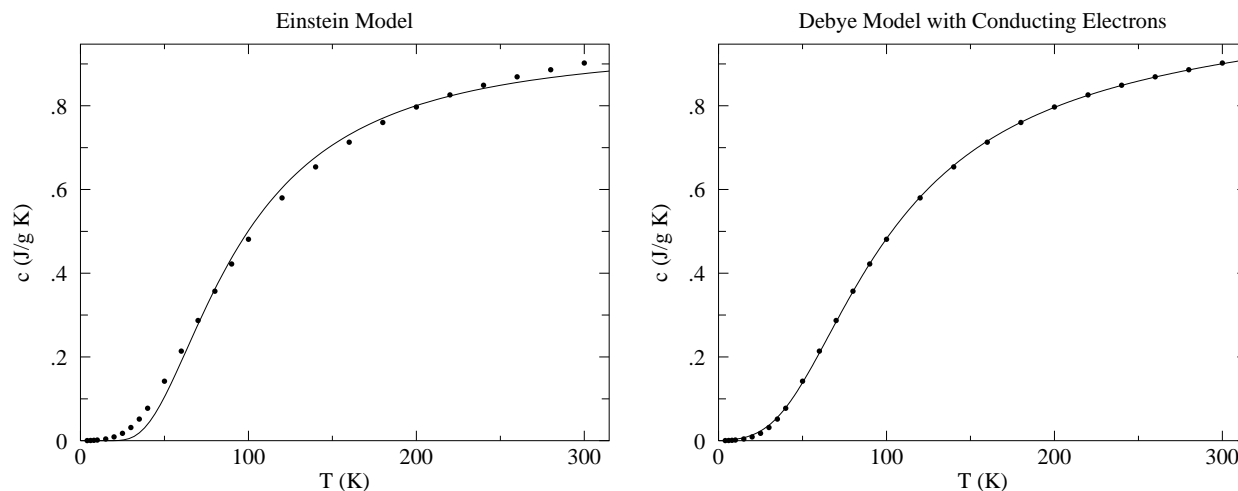
Figure 1: Aluminum specific heat compared to the models of Einstein and Debye.

Atoms actually have very complex and unexpected interactions, so physicists often create simplified versions of atoms ('models') that allow easy calculation and display aspects of real material behavior. In this lab you will deal just with the simplest models of the behavior of atoms in solids, but you should know that we've found a seemingly unending cornucopia of surprising macroscopic behavior caused by very subtle atomic behavior (e.g., superconductivity).

Einstein's model[2] postulated that in a solid the atoms were stuck more or less in place by strong interatomic forces but those atoms could vibrate, like simple harmonic oscillators, about their equilibrium positions. Since the atoms were identical they all shared a common vibration angular frequency, ω_E. If classical mechanics was applied to these atoms, one could show that the molar specific heat would be $3R$ (independent of temperature), where R is the gas constant. In fact about a century earlier Dulong & Petit had experimentally found that to be the case near room temperature. But as noted above the Laws of Thermodynamics require specific heats to approach zero at low temperatures. When Einstein applied the energy quantization discovered by Planck (1900) to his model solids, he found exactly was was needed: at room temperature the molar specific heat would be $3R$, but at low temperatures[3] the specific heat would approach zero. His result for molar specific heat, C, can be expressed most conveniently in terms of the Einstein temperature: $T_E = \hbar\omega_E/k_B$:

$$C(T) = 3R \, (T_E/T)^2 \, \frac{e^{T_E/T}}{(e^{T_E/T} - 1)^2} \tag{3}$$

Low mass atoms connected by stiff springs would have high T_E (like diamond $T_E \sim 1800\ K$) whereas heavy atoms with soft springs would have low T_E (like lead $T_E \sim 85\ K$). In this lab you will be working with aluminum: $T_E \sim 300\ K$. If $T \gtrsim T_E$ the specific heat is approximately constant ($\pm10\%$).

Debye[4] improved Einstein model by noting that there should additionally be much lower frequency collective modes, that would resemble long wavelength sound waves. Including an infinity of new modes (up to an angular frequency ω_D) makes a much more complex model, but as shown in Fig. 1, produces a much better fit to experiment. Additionally metals have 'free' electrons whose kinetic

---

[2]A. Einstein, Ann. Physik **22**, 180 & 800 (1907)

[3]Machines that could create 'cryogenic' low temperatures were built by Kamerlingh Onnes who received the Nobel prize for this work in 1913.

[4]P. Debye, Ann. Physik **39**, 789 (1912)

Properties of Boiling N_2		Properties of Room Temperature Al	
Temperature, T_{BP}:	77 K	Temperature, T_{RT}:	
Density:	$0.81 \text{ g} \cdot \text{cm}^{-3}$	Density:	$2.67 \text{ g} \cdot \text{cm}^{-3}$
Latent Heat, L:	$199 \text{ J} \cdot \text{g}^{-1}$	Specific Heat, c:	$0.90 \text{ J} \cdot \text{g}^{-1} \cdot K^{-1}$
Vapor Mass, Δm:		Mass, m:	

Table 1: Material properties and symbol definitions.

energy should be added to the vibrational energy. Debye's model is an improvement in recognizing the existence of these slow frequency oscillations modes, but it is not exactly correct: the collective behavior of atoms in solids has proven to have a seemingly unending complications, and hence unending fun for physicists.

In 1897 an alternative to model-building was pushed by Ernst Mach[5]. He argued that physicists should simply make and record measurements, basically because (aside from rare experimental blunders) the results are actually true[6] and are what is needed to make useful stuff (like steam engines). Even if the imagined microscopic mechanism were true (he was skeptical) they would not much help engineering progress.

The limited horizon offered to physicists by Mach is not very appealing to me. I love thinking I know the cause of superconductivity, even if the theory is of little use in making superconductors. In the case at hand we can keep score on the accuracy of Debye's guesses: vibrating atoms: check, quantum mechanics: check, low frequency modes: check. Now with modern technology we can actually measure the low frequency modes and we find that while they resemble those hypothesized by Debye, there are striking differences. Hence if measured sufficiently accurately, experiment would not exactly match Debye's theory. Now it has to be said that not all theories are as successful as Debye's; the scientific literature is filled with theories that did not work out.

Lab Objective: Measure the latent heat of vaporization of liquid nitrogen and estimate the Einstein temperature of aluminum.

In theory, measuring the latent heat of vaporization of nitrogen, L, is easy: Drop a room temperature mass of aluminum into the nitrogen. As the aluminum cools from room temperature (T_{RT}) to 77 K (T_{BP}), it will release an amount of heat, H. If we measure the mass of vapor produced (Δm), the latent heat, $L = H/\Delta m$. One might now be temped to say the heat comes from aluminum so $H = mc(T_{\text{RT}} - T_{\text{BP}})$, but we now know that the specific heat of aluminum is not even approximately constant over such a large temperature range, so we must work a bit harder. If we pull the cold aluminum from the nitrogen and submerge it in water (mass M), a final equilibrium temperate, T_f will be reached. Again one might be tempted to conclude that the heat lost from the water and absorbed by the aluminum ($Mc_w(T_{\text{RT}} - T_f)$) matches the heat H given up to the nitrogen when the aluminum was cooled, but in the water the aluminum just moved from T_{BP} to T_f, not the aluminum's actual temperature change when giving up H (which was $T_{\text{RT}} \to T_{\text{BP}}$) So we must include a calculated heat to move the aluminum from T_f all the way back to T_{RT}, so

$$H = Mc_w(T_{\text{RT}} - T_f) + mc(T_{\text{RT}} - T_f) = (Mc_w + mc)(T_{\text{RT}} - T_f) \tag{4}$$

---

[5]Best known for Mach numbers describing supersonic flow.

[6]The history of measuring the specific heat of hydrogen shows this is not simple, See: C. A. Gearhart, Arch. Hist. Exact Sci. **64** 113-202, (2010). As Todd says: "Don't trust Experiment that hasn't been confirmed by Theory".

(Between T_f and T_{RT} the temperature change is so small we can assume the specific heats are constant.)

So needed data: $M, m, \Delta m, \Delta T = T_{\mathrm{RT}} - T_f$

There is a complication. It seems easy to measure Δm: just weigh the liquid nitrogen before and after the boiling. However the mass of the nitrogen is continuously decreasing (due to heat leaking into the dewar). If we were to use a simple before minus after calculation, we would be including both vaporization due to the aluminum heating and due to the general heat leak. The plan is to continuously monitor the nitrogen mass from 10 minutes before the aluminum has bee added to 10 minutes after vigorous boiling has stopped. The result would looks like Fig. 2, and Δm would be the separation between the before and after loss-lines.

One more complication: if the nitrogen loss rates were the same before aluminum insertion and after vigorous boiling, the separation between the parallel lines could be taken at any location. However, this is usually not the case (the vigorous boiling cools the inside of the dewar, so the after situation is not the same as the before situation). The logical place to measure the distance between the lines is at the mid-point of the boiling. So use WAPP to determine the before line using the data 4 minutes before aluminum insertion, and do the same for the 4 minutes after vigorous boiling and then calculate the difference between the lines at the boiling midpoint. The error in Δm can be estimated by following the same procedure but using the time of aluminum insertion and again at the end of vigorous boiling, and then applying the high-low method to these two extreme measures of Δm.

Comment: Often thermodynamic calculations assume a slow, quasi-equilibrium process. But this lab has violent processes far from equilibrium. For example usually ice will form on the newly submerged aluminum, and often the thermometer will get frozen into the ice. The final temperature should be taken only after all the ice has melted and the water stirred (e.g., by stirring with the aluminum hunk itself) so the liquid water+aluminum system has reached equilibrium. All of this out-of-equilibrium behavior does not invalidate your calculations because they involve *state functions* like energy (or more accurately enthalpy).

You will collect liquid nitrogen mass, calorimeter temperature, and time data using the program LN2 on a raspberry pi. The balance reports 10 weights per second. The program continuously averages 300 weight measurements and reports that average along with the maximum and minimum weights during that 30 seconds. The calorimeter temperature is is measured by a DS18B20 sensor and printed by the program at the end of each 30 second interval.

Materials

USS-DBS28-30 balance (accuracy 0.02 g)
DS18B20 thermometer (accuracy 0.3 °C)
Aluminum cylinder attached to string
Dewar with ~ 150 g liquid nitrogen
Styrofoam cup with ~ 130 g <u>distilled</u>, room temperature water
Raspberry Pi

Lab

Weigh the aluminum cylinder (m); tare then fill the styrofoam cup with ~ 130 g distilled water (M); tare then fill the dewar with ~ 150 g liquid nitrogen; cap the dewar. Place the aluminum cylinder and the dewar on the weighing pan; start the program. The data should show a slowing evaporating
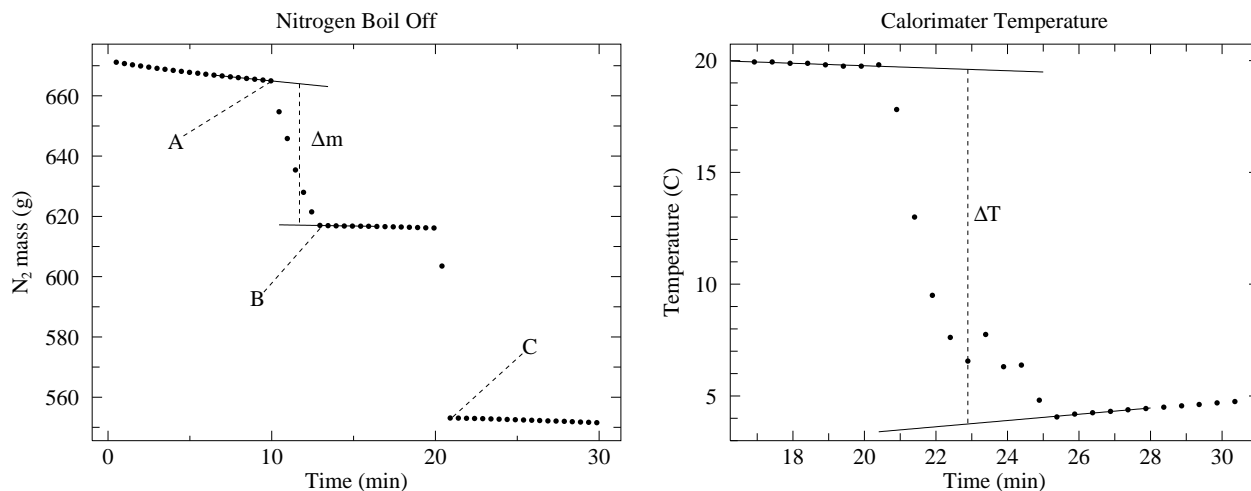
Figure 2: A: aluminum moved into liquid nitrogen and vigorous boiling begins, B: vigorous boiling stops, C: aluminum transferred to calorimeter. Note where/how Δm was determined. When stirred the calorimeter temperatures changes can reverse. You must stir until the ice has detached from the aluminum and melted so equilibrium is assured. Note where/how ΔT was determined.

mass of liquid nitrogen. After about 10 minutes, carefully move/drop the aluminum cylinder into the dewar; Vigorous boiling should start; recap the dewar. After about 3 minutes the boiling will essentially stop as shown by an almost unchanging nitrogen mass. With the now cold aluminum sitting in the nitrogen, wait ~ 5 minutes. Quickly transfer the now cold aluminum into the calorimeter's water. Ice will immediately encase the aluminum and vapor will be produced. Over the following ~ 5 minutes the calorimeter temperature will fall, perhaps irregularly as you stir the water. Once all the ice has melted and the calorimeter seems to be at equilibrium (as shown by a constant slow increase in its temperature), you can determine the ΔT of the water.

As described above, the mass of nitrogen vaporized is found by extrapolating the before-insertion loss rate line and the post-boiling loss rate line to the mid-point of the boiling. Given this Δm the latent heat of vaporization, L, can be calculated:

$$L = \frac{H}{\Delta m} \tag{5}$$

The average specific heat of aluminum between T_{BP} and T_{RT} is

$$\overline{c} = \frac{H}{m(T_{\mathrm{RT}} - T_{\mathrm{BP}})} \tag{6}$$

The average specific heat is less than the room temperature specific heat; Einstein's model has been used to calculate the ratio of the average specific heat to the specific heat at 300 K. Calculate that ratio ($\overline{c}/c(300)$) and use Fig. 3 to estimate the Einstein temperature of aluminum.

Make hardcopy plots[7] similar to those in Fig. 2. WAPP 4 minutes of nitrogen mass data both before insertion and after boiling. Record both A, B WAPP results. Note: given the high accuracy of the

---

[7]For data point plotting: copy&paste into http://www.physics.csbsju.edu/plot/WAPP2PLOT.html, but note on linux Ctrl-C kills not copies; highlight and right mouse click to copy.
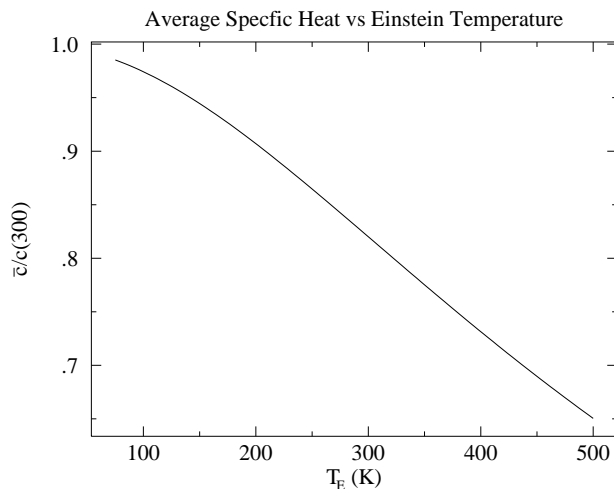
Figure 3: The average specific heat between 300 K and 77 K, $\overline{c}$ (relative to the specific heat at 300) as a function of an assumed Einstein temperature.

balance, there is no need to include error in balance reported masses. Using the fit linear functions, calculate the nitrogen mass at the boiling midpoint, and at the before/after extreme times[8]. Calculate Δm and its error. As above use before/after WAPP fits to calculate ΔT and its error. Record both A, B WAPP results. Calculate L and its error. Calculate $\overline{c}/c(300)$ (no error) and using Fig. 3, estimate the resulting T_E.

Appendices

$\overline{c}/c(300)$ in the Einstein model:

In the Einstein model the molar internal energy is given by:

$$U(T) = \frac{3RT_E}{e^{T_E/T} - 1} \tag{7}$$

so the average molar specific heat is

$$\overline{C} = \frac{U(T_{\mathrm{RT}}) - U(T_{\mathrm{BP}})}{T_{\mathrm{RT}} - T_{\mathrm{BP}}} \tag{8}$$

If we now divide that by the specific heat at room temperature, and simplify a bit we get:

$$\frac{\overline{c}}{c(T_{\mathrm{RT}})} = \frac{T_{\mathrm{RT}}^2}{T_E} \, e^{-T_E/T_{\mathrm{RT}}} \, \frac{e^{T_E/T_{\mathrm{BP}}} - e^{T_E/T_{\mathrm{RT}}}}{T_{\mathrm{RT}} - T_{\mathrm{BP}}} \, \frac{e^{T_E/T_{\mathrm{RT}}} - 1}{e^{T_E/T_{\mathrm{BP}}} - 1} \tag{9}$$

in short, kind of a mess.

USS-DBS28-30 balance modes/details

Calibration (probably not needed for this lab)

Press and hold the TARE/CAL key. Wait for − CAL − to be displayed followed by 2000.00 (blinking). Put 2 kg on the balance and wait until the blinking stops. Remove the 2 kg.

---

[8]The 'cgi calculator' on www.physics.csbsju.edu allows you to calculate the value of a function at several points with one click.

Serial Reports

The balance reports weights serially at 9600 baud. 15 characters are sent followed by CR/LF. The first character is either + or −; the 10th character is a period; the last 3 characters are the unit e.g., g␣␣; the remaining characters denote the value and are numerals (0123456789) or leading spaces. Example: -␣␣␣␣␣␣␣0.11g␣␣

Continuous Serial Reports Mode (at 10 Hz)

Press/hold COU key; −COU− displayed (continue to hold); 10 will appear and blink (continue to hold), finally CO − off is displayed. Press/repeat TARE/CAL key until C5-x appears (value of x doesn't matter). Press/repeat COU key until C5-0 appears. Press TARE/CAL key twice (will appear to change C5-0 but no worries).

Single Serial Report Mode

Proceed as above, but on the return to the COU key, press until C5-2 appears; Finish with two presses of TARE/CAL key (as above). Now pressing the UNIT key forces a serial report.

Looking for More Fun?

Consider using a different material. Lead has a smaller T_E; silicon has a larger T_E.
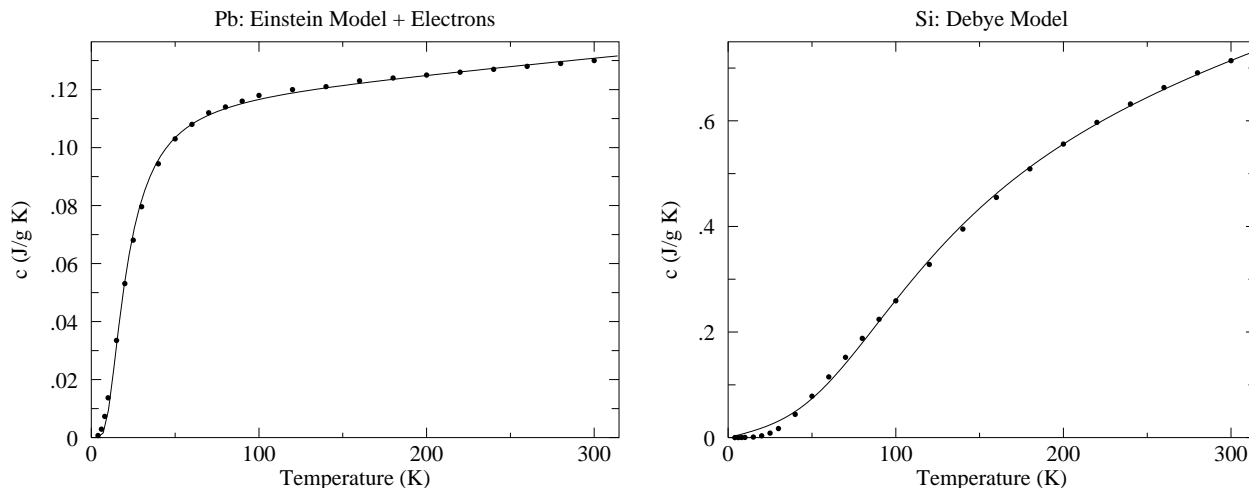

Figure 4: If you want to try a different material we have sample of lead and silicon available.