Physics 317 – Chowdary
Thermodynamics and Statistical Physics
Fall 2005

Homework #25, due Mon. Oct. 31

Computer Exercise #4 (below),

6.23 (keep as many terms as you need for the sum to converge), 6.26 (no need to sketch), 6.31

Computer Exercise #4
Rotational Partition Function and Heat Capacity

In this Computer Exercise, you'll use a computer to help you calculate the rotational partition function. You'll also use the computer to calculate the average energy per particle, as well as calculating and plotting the heat capacity per particle. Our goal is to develop a graph of the heat capacity per particle vs. (reduced) temperature that shows the low temperature, intermediate temperature, and high temperature behavior.

Background

For a diatomic molecule made of distinguishable atoms like CO or HCl, the allowed rotational energies are quantized: $E(j) = j(j+1)\varepsilon$ where $j = 0,1,2,\ldots$ and ε is some constant that is inversely proportional to the molecules moment of inertia. The number of different states with the same energy $E(j)$ is the degeneracy of the state j. We call this degeneracy $g(E(j)) = 2j+1$.

So the partition function associated with the rotational energy levels ("the rotational partition function") is $Z_{rot} = \sum_s e^{-\beta E(s)} = \sum_E g(E)e^{-\beta E} = \sum_{j=0}^{\infty}(2j+1)e^{-\beta j(j+1)\varepsilon}$. Recall that $\beta \equiv 1/kT$.

High Temperature Limit

In the limit that $kT >> \varepsilon \Rightarrow kT/\varepsilon >> 1$ or equivalently $\beta << \varepsilon \Rightarrow \beta\varepsilon << 1$, this sum is well approximated by an integral, and we get the results summarized in eqs. (6.31) and (6.32).

This analysis can also extend to diatomic molecules with identical atoms or even polyatomic atoms; in those cases you need to adjust the partition factor to account for any symmetries (see the discussion preceding Problem 6.23 on p. 236).

General Solution

In the low temperature limit, the sum in the partition function can't be approximated by an integral. So we must explicitly carry out the sum. The advantage is that we usually don't have to carry out too many terms in the sum, since each successive term gets smaller and smaller. And doing an explicit summation will also give us the high temperature behavior as well. To start, we'll sum up to and including the $j = 6$ level.

This is ideally suited for a symbolic manipulation program like Mathematica. If you'd like to use another program like Maple, please feel free. This is not a task for which a spreadsheet program like Excel is suited. I've given you the core Mathematica commands that you will need to use; for those of you with experience in Mathematica you should feel free to modify the core commands as you see fit. Mathematica is extremely powerful, but it is also very finicky, so you must make sure to type in exactly what I have provided you. To execute a command ("evaluate a cell"), hit Enter on the numeric keypad or Shift+Enter on the keyboard.

Mathematica Commands

Begin by typing

```
z = Sum[(2 j + 1) Exp[-j (j + 1) * b * eps], {j, 0, 6}]
```

Here, `b` is β and `eps` is ε. I hope the rest of the syntax is self explanatory. Evaluate this cell.

Next, type

```
energy = -(1 / z) * D[z, b] /. b → 1 / (k * T)
```

Here, `D[z, b]` is $\frac{\partial Z}{\partial B}$, so that `energy` is the average energy per particle.

The last part, `/.b → 1/(k*T)` is a little obscure. After the derivative is taken, this command replaces every instance of `b` with `1/(k*T)`.

<u>Question:</u> Why might we want to replace every instance of `b` with `1/(k*T)`? (Hint: consider how we'll obtain the heat capacity per particle from the average energy per particle.)

Next, type

```
heatcap = D[energy, T] /. T → t * eps / k
```

Here, `heatcap` is the heat capacity per particle, and `D[energy, T]` is $\frac{\partial \bar{E}}{\partial T}$.

The `/.T → t*eps/k` in this line is simply for sake of being able to plot in reduced temperature $t = kT/\varepsilon$, as we've done many times before.

Finally, type

```
Plot[heatcap / k, {t, 0.0001, 3}, PlotRange → {{0, 3}, {0, 1.2}}, Frame → True
```

to plot the dimensionless heat capacity per particle vs. the reduced temperature.

Analysis

1) Submit a clear, attractive version of this plot (an electronic version is fine). Make sure the axes are labeled.

2) Comment on the "high" temperature behavior. Does it display the value you expect? Briefly discuss.

3) Comment on the low temperature behavior. Does this match your expectations from the Third Law of Thermodynamics?

4) Look at the graph around the region $t = 1$, which corresponds to $kT = \varepsilon$. What do you notice about the value of the heat capacity per particle, especially compared to the high temperature limit?

5) Did we calculate enough terms in the partition function? Do we need more? Could we have gotten away with less? Go to the first line, and change the 6 to 7; evaluate all the cells again. Does the graph change noticeably? Next, reduce to 5, then 4, etc. What's your conclusion about the minimum number of terms we should calculate in the partition function over the range of reduced temperatures we are plotting?

6) Go back to the first line, and return the value to 6 (remember to evaluate the cell). Now, go to the Plot line, and increase the 3 in both places until you can see the "high" temperature behavior deviate from its expected value. What can you conclude from this?