

Problem 6.10. A water molecule can vibrate in various ways, but the easiest type of vibration to excite is the “flexing” mode in which the hydrogen atoms move toward and away from each other but the HO bonds do not stretch. The oscillations of this mode are approximately harmonic, with a frequency of 4.8×10^{13} Hz. As for any quantum harmonic oscillator, the energy levels are $\frac{1}{2}hf$, $\frac{3}{2}hf$, $\frac{5}{2}hf$, and so on. None of these levels are degenerate.

- (a) Calculate the probability of a water molecule being in its flexing ground state and in each of the first two excited states, assuming that it is in equilibrium with a reservoir (say the atmosphere) at 300 K. (Hint: Calculate Z by adding up the first few Boltzmann factors, until the rest are negligible.)
- (b) Repeat the calculation for a water molecule in equilibrium with a reservoir at 700 K (perhaps in a steam turbine).

Problem 6.10

```
In[1]:= Clear["Global`*"]
In[2]:= f = Quantity[4.8*1013, "Hertz"];
        h = Quantity[1, "PlanckConstant"];
        k = Quantity[1, "BoltzmannConstant"];
In[5]:=  $\epsilon[n_] := \left(n + \frac{1}{2}\right) h f$ 
In[6]:=  $\beta[T_] := 1 / (k * T)$ 
In[7]:= UnitConvert[ $\epsilon[0]$ , "Electronvolts"]
Out[7]= 0.099256 eV
```

(a) T = 300 K

```
In[8]:= T = Quantity[300, "Kelvins"];
In[9]:= UnitConvert[1. /  $\beta[T]$ , "Electronvolts"]
Out[9]= 0.025852 eV
```

How many terms should we include in the partition function sum? Look at successive terms -- each energy level is $n' * h f$.

```
In[10]:= Table[{n, Exp[-β[T] × ε[n]]}, {n, 0, 10}] // TableForm
```

```
Out[10]//TableForm=
0      0.0215066
1      9.94756 × 10-6
2      4.60109 × 10-9
3      2.12816 × 10-12
4      9.8435 × 10-16
5      4.55296 × 10-19
6      2.1059 × 10-22
7      9.74053 × 10-26
8      4.50533 × 10-29
9      2.08387 × 10-32
10     9.63864 × 10-36
```

Clearly just the first few terms are important. Pick '5' as an arbitrary but conservative number of terms to keep.

```
In[11]:= Z = Sum[Exp[-β[T] * ε[n]], {n, 0, 5}]
```

```
Out[11]=
0.0215166
```

```
In[12]:= prob[n_] := 
$$\frac{\text{Exp}[-\beta[T] * \epsilon[n]]}{Z}$$

```

```
In[13]:= Framed[TableForm[Table[{n, prob[n]}, {n, 0, 2}],
  TableHeadings → {None, {"State", "Probability"}}]]
```

```
Out[13]=
```

State	Probability
0	0.999537
1	0.000462321
2	2.13839×10^{-7}

(b) T = 700 K

```
In[14]:= T = Quantity[700, "Kelvins"];
```

```
In[15]:= UnitConvert[1. / β[T], "Electronvolts"]
```

```
Out[15]=
0.0603213 eV
```

How many terms should we include in the partition function sum now?

```
In[16]:= Table[{n, Exp[-β[T] × ε[n]]}, {n, 0, 10}] // TableForm
```

```
Out[16]//TableForm=
```

```
0      0.192925
1      0.00718066
2      0.000267264
3      9.94756 × 10-6
4      3.70248 × 10-7
5      1.37806 × 10-8
6      5.12914 × 10-10
7      1.90907 × 10-11
8      7.10554 × 10-13
9      2.64468 × 10-14
10     9.8435 × 10-16
```

Clearly just the first few terms are important, but to get the same accuracy as before, we need to go up to at least 10 terms.

```
In[17]:= Z = Sum[Exp[-β[T] * ε[n]], {n, 0, 10}]
```

```
Out[17]=
```

```
0.200383
```

```
In[18]:= prob[n_] := 
$$\frac{\text{Exp}[-\beta[T] * \epsilon[n]]}{Z}$$

```

```
In[19]:= Framed[TableForm[Table[{n, prob[n]}, {n, 0, 2}],
  TableHeadings → {None, {"State", "Probability"}}]]
```

```
Out[19]=
```

State	Probability
0	0.96278
1	0.0358347
2	0.00133377