Classwork 1: A toy thermodynamic system

16 January 2012

In this classwork we’re going to consider a “toy” thermodynamic system, to get a feel for microstates and macrostates. First, though, we need to revise some counting problems.

1. Counting and statistics

   Permutations are arrangements of objects where the order matters – in statistical physics, this corresponds to distinguishable particles, such as in a solid.

   a. First consider two distinguishable objects – for example, kittens. There are two ways of arranging them in order: kitten A then kitten B, or vice versa.

   Now consider three kittens: how many ways of arranging them are there now (hint: it’s not three)? What if there were four kittens? One way of thinking about this is to see how many ways there are of picking the first kitten, then how many there are left to pick for the second, and so on.

   What if there were \( N \) kittens: how many ways are there of arranging them in order?

   b. We now want to distribute the kittens into two baskets, with \( n \) in one and \( m \) in the other, such that \( n + m = N \). We don’t mind the order in which they’re put in each basket – this is a combination rather than a permutation. How many ways are there of distributing the kittens in this way?

   Hint: think about how many ways you can arrange \( n \) kittens: there are that many fewer ways of arranging the whole set if we’ve put \( n \) of them into one basket.

   c. Finally, if there were \( i=1...k \) different baskets, each with \( n_i \) kittens in them, how many ways are there of distributing them?

   In terms of statistical physics, the kittens could be atoms and each basket holds all the atoms with a particular amount of energy. What we’ve done here is work out how many ways – the statistical weight, \( \Omega \) – there are of arranging the atoms in this particular way. We’ll need this formula in the next question.

2. A simple system

   Let’s see how this works for a toy system, first discussed by Boltzmann in 1877.

   We have seven identical atoms, each of which can vibrate as a simple harmonic oscillator with energies quantised as 0, \( \varepsilon \), 2\( \varepsilon \), 3\( \varepsilon \), etc.

   However, we have a constraint: the total energy of the system is 7\( \varepsilon \). This means that there are limits on how much energy the atoms can have.

   We define \( n_0 \) as the number of atoms with energy 0, and so on:

   \[
   \begin{align*}
   n_0 & \text{ atoms have energy } 0 \\
   n_1 & \text{ atoms have energy } \varepsilon \\
   \vdots & \text{ } \vdots & \text{ } \vdots \\
   n_7 & \text{ atoms have energy } 7\varepsilon 
   \end{align*}
   \]
We have two constraints: the number of particles is 7 and the total energy is $7\varepsilon$:

$$\sum_{i=1}^{7} n_i = 7 \quad \text{and} \quad \sum_{i=1}^{7} n_i \varepsilon_i = 7.$$ 

a. Write down a table in the following format, with all the possible ways of distributing the energy between the particles. There are 15 in total.

The right-most column is to save you time for part (b); leave it blank for now.

I’ve filled in three rows already. The first corresponds to 6 atoms with zero energy and one with $7\varepsilon$. The last has all seven atoms with $\varepsilon$ energy. Make sure you understand the notation: to what state does the second row correspond?

<table>
<thead>
<tr>
<th>$n_0$</th>
<th>$n_1$</th>
<th>$n_2$</th>
<th>$n_3$</th>
<th>$n_4$</th>
<th>$n_5$</th>
<th>$n_6$</th>
<th>$n_7$</th>
<th>$\Omega$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>15</td>
<td>0</td>
<td>7</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Fill in all 15 cases (it’s surprisingly quick to do), making sure that you always have 7 particles, and a total of $7\varepsilon$ of energy, in each row.

b. Now think about what you’ve done: subject to the constraints on energy and particle number, you’ve worked out all the different **macrostates** that are possible: each has a different distribution of the energy between the atoms. However, there are more ways of getting some of these arrangements than others – in other words, they have more corresponding **microstates**.

Now, we can work out the number of microstates that corresponds to each of these macrostates. This is the number of ways of arranging $N$ distinguishable objects into sets, where the order is unimportant, which as we saw is given by:

$$\Omega(N, n_0, n_1, \ldots, n_k) = \frac{N!}{n_0! n_1! \cdots n_k!}$$

Calculate this for each of the 15 arrangements in the table above and fill it into the right-most column. Remember, $0! = 1$ and try to be efficient when you calculate the products.

c. Assuming that every microstate is equally probable (the fundamental postulate for an isolated system), which macrostate is most likely to occur? What is the distribution of energies between atoms for this state? Does this remind you of anything?
**Classwork 2: Work and heat**  
27 January 2012

Today, we’re going to see how we can interpret work and heat from a statistical point of view and see how that relates to thermodynamics.

I am deliberately *not* giving you the expressions that you need to start from: they are in your notes and in any case you need to start remembering them! If you can’t remember, ask a demonstrator.

We consider a system in thermal equilibrium with a heat bath: $T$ and $N$ are constant, but $U$ can vary and, importantly, for this example so can the volume $V$.

a. Write down an expression for the energy $U$ of a system in terms of energy levels and the probabilities of it occupying those levels. What is the generalised differential of this in terms of both $dp_i$ and $d\varepsilon_i$? We now aim to work out each of these terms individually.

b. Re-arrange the Boltzmann probability distribution function to obtain $\varepsilon_i$ in terms of $Z$ and $p_i$.

c. From the expression for the Gibbs entropy of a canonical distribution and using your answer to part (b), show that one of the terms of the differential form of $U$ from part (a) is actually $TdS$.

We now consider the other term of $dU$, which concerns changes in energy levels. Such a change can only occur if the configuration of the system changes in some way, not just by adding energy to it. Here, the only way for the configuration to change is if the volume changes, so we can write

$$d\varepsilon_j = \frac{d\varepsilon_j}{dV} dV .$$

d. Write down the first law of thermodynamics and the expression for the free energy, $F$. Show that the differential form of $F$ can be written

$$dF = -pdV - SdT .$$

Therefore, we can write

$$P = -\left(\frac{\partial F}{\partial V}\right)_T .$$

e. From the relation between $F$ and $Z$ and using your answer above, show that

$$\left(\sum_j \frac{d\varepsilon_j}{dV} p_j\right)dV = -PdV .$$

f. Hence, show that

$$dU = TdS - PdV .$$
Classwork 3: The diatomic classical gas

3 February 2012

In section 6.3 of the lecture notes we derived the partition function of a monatomic classical ideal gas. We mentioned degeneracy of energy levels, but did not treat them in detail. In this classwork, we’re going to look at the more complex case of a diatomic molecule and see how this affects the partition function and some macroscopic thermodynamic properties.

The most obvious contribution to the energy of a molecule is its translational (kinetic) energy $\varepsilon_{tr}$, which is the only one that we have considered up to now. However, there are quite a few more: you might want to spend a moment and see how many you can think of – without looking at the rest of this sheet!

One key assumption that we’re going to make is that the different contributions to the energy are independent of each other – so rotational and vibrational modes don’t interact, for example. In practice this is well satisfied. We will see how we can combine their effects to get the overall properties of the system.

a. The total energy of a single diatomic molecule can be written $\varepsilon = \varepsilon_{tr} + \varepsilon_r + \varepsilon_v + \varepsilon_e + \varepsilon_n$ for the translational, rotational, vibrational, electronic and nuclear contributions. Write down the general formula for a single particle partition function $Z$ without degeneracy and hence show that we can write

$$Z = Z_{tr}Z_rZ_vZ_eZ_n.$$ 

Importantly, since it is $\ln Z$ that we use in thermodynamic calculations, this means that the different elements of the partition function are additive.

b. Rotational modes. The molecule can rotate about its centre of mass. The quantum mechanical energy levels of a rigid rotator are

$$\varepsilon_j = j(j+1)\frac{\hbar^2}{2I}, \quad j = 0,1,2,...$$

where I is the moment of inertia. These levels have degeneracy $g_j=2j+1$. Write down the partition function $Z_r$ for the rotational modes, including degeneracy. It’s helpful to define the characteristic temperature $\theta_r = \frac{\hbar^2}{2I k_B}$ in the same way that we did for the harmonic oscillator in problem sheet 2. This is about 15K for a HCl molecule and 85K for H$_2$.

If $T \ll \theta_r$, what state is the molecule likely to be in, and how can $Z_r$ be simplified? Given that the mean energy for a particle $< E > = -(\partial \ln Z / \partial \beta)_{T,N}$, what is $< E >$ for the rotational modes at low temperatures?

If $T \gg \theta_r$, we can consider the molecule to be moving between so many states that we can treat them as a continuum and convert our sum over $j$ to an integral,

$$Z_r = \int_{0}^{\infty} (2j+1)e^{-j(j+1)\frac{\theta_r}{T}} dj.$$ 

Use the substitution $x=j(j+1)$ to show that when $T \gg \theta_r$, (... turn over...)
Z_v = \frac{T}{\theta_v} = \frac{2I}{\beta \hbar^2}.

What is \langle E \rangle for the rotational modes at high temperatures?

c. Vibrational modes. The molecular bond can vibrate and we can treat this as a harmonic oscillator. Write down the partition function \( Z_v \) for a harmonic oscillator (see section 3.3 and problem sheet 2; you can use your answers from there). Again it’s useful to define the characteristic temperature \( \theta_v = \hbar \omega / k_B \).

What is \langle E \rangle for temperatures far above and below \( \theta_v \)?

In practice, \( \theta_v \) is often large – for example, it is 4130K for a HCl molecule. What does this tell you about which vibrational modes are excited at room temperature?

c. Electron excitation. Electrons can be excited to higher energy levels by thermal energy. We can write the partition function for this as

\[ Z_e = \sum_j g_j e^{-\beta \epsilon_j} \]

where \( g_j \) is the degeneracy of energy level \( j \). To get an idea of the effect of this for room-temperature systems, work out the thermal temperature required to ionise a hydrogen atom. Explain why we can therefore write the electron partition function as \( Z_e = g_e \), where \( g_e \) is the degeneracy of the lowest electron energy level.

d. Nuclear effects. This is a very easy one: the binding energies in the nucleus are so large that their characteristic temperature is far higher than room temperature. We can therefore ignore them completely and write \( Z_n = g_n \), where \( g_n \) is the degeneracy of the lowest nuclear level.

e. We can now put all this together to get the total single partition function. It’s tedious to write out so let’s simplify it by putting all the internal degrees of freedom together as \( Z_{\text{int}} = Z_v, Z, Z_e, Z_n \). Note too that \( Z_{\text{int}} \) is independent of volume (why?). Using the single particle translational partition function from section 6.3, show that the full partition function of \( N \) particles is

\[ Z = \frac{1}{N!} \left( \frac{2 \pi m k_B T}{\hbar^2} \right)^{3N/2} \nu^N Z_{\text{int}}^N \]

Hence show

\[ \ln Z = N \left( \ln \nu + \frac{3}{2} \ln k_B T + \frac{3}{2} \ln \frac{2m}{\hbar^2} + \ln Z_{\text{int}} - \ln N + 1 \right) \]

and \( U = +k_B T^2 (\partial \ln Z / \partial T)_{\nu, N} = 3/2 Nk_B T + Nk_B T^2 (\partial \ln Z_{\text{int}} / \partial T)_{\nu, N} \).

This shows that the total internal energy can be affected by the internal degrees of freedom, as we expect, but constants such as \( g_e \) have no effect. Finally, based on what you have calculated, plot the molar heat capacity \( C_V \) of the diatomic gas as a function of temperature, from the boiling point to above both \( \theta_r \) and \( \theta_v \), noting points of interest.
Statistical physics
Classwork 1
Answers.

1. a. Two kittens (distinguishable)
   2 ways to arrange them:
   1 A B
   2 B A

   3 kittens: 6 ways
   N kittens: N! ways.

   b. Answer: \[
   \frac{N!}{n! \times m!} = \frac{N!}{m!} \frac{1}{n!}
   \]

   This is because, of the N! ways of arranging N objects, a factor of n! of them are now effectively the same answer, as our n objects are indistinguishable. Similarly for m.

   c. Answer: \[
   \Omega = \frac{N!}{n_1! \times n_2! \times \ldots} = \frac{N!}{m!} \prod_{i=1}^{n} \frac{1}{n_i!}
   \]

   In terms of atoms with different energies:
   We have N atoms, \( n_i \) have energy \( \varepsilon_i \), and so on. The number of microstates, \( \Omega \), is given by
   \[
   \Omega = \frac{N!}{\prod_{i=1}^{n} n_i!}
   \]
2. \( N = 7, \quad \Sigma \eta_i \)
\( U = 7 \Sigma \xi \Omega \cdot \eta_i \).

<table>
<thead>
<tr>
<th>( \eta_0 )</th>
<th>( \eta_1 )</th>
<th>( \eta_2 )</th>
<th>( \eta_3 )</th>
<th>( \eta_4 )</th>
<th>( \eta_5 )</th>
<th>( \eta_6 )</th>
<th>( \eta_7 )</th>
<th>( \Omega )</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>7</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>42</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>42</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>42</td>
</tr>
<tr>
<td>5</td>
<td>4</td>
<td>1</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>105</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>0</td>
<td>2</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>105</td>
</tr>
<tr>
<td>7</td>
<td>4</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>210</td>
</tr>
<tr>
<td>8</td>
<td>4</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>105</td>
</tr>
<tr>
<td>9</td>
<td>3</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>140</td>
</tr>
<tr>
<td>10</td>
<td>3</td>
<td>1</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>140</td>
</tr>
<tr>
<td>11</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>420</td>
</tr>
<tr>
<td>12</td>
<td>2</td>
<td>4</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>105</td>
</tr>
<tr>
<td>13</td>
<td>2</td>
<td>3</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>210</td>
</tr>
<tr>
<td>14</td>
<td>1</td>
<td>5</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>42</td>
</tr>
<tr>
<td>15</td>
<td>0</td>
<td>7</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>

b. \( \Omega \)'s in the table above.
Quite quick if you pre-calculate: \[ \Omega = \frac{N!}{\eta_0! \eta_1! \ldots} \]
Example state 12: \[ \Omega = \frac{5040}{2 \times 24} \]
\[ 0! = 1 \]
\[ 1! = 1 \]
\[ 2! = 2 \]
\[ 3! = 6 \]
\[ 4! = 24 \]
\[ 5! = 120 \]
\[ 6! = 720 \]
\[ 7! = 5040 \]
c. Most likely state is $R = 420$:
\[ n_0 = 3, \ n_1 = 2, \ n_2 = 1, \ n_3 = 1. \]

Looks like a decaying exponential
- Boltzmann distribution
\[ n_i \propto e^{-\frac{E_i}{kT}} \]

This is what we would expect from what we
saw in the lectures; works quite well even
for such a small system ($N=7$)!
STATISTICAL PHYSICS
CLASSWORK 2

a. \[ U = \sum_j \varepsilon_j p_j \]

\[ \Rightarrow \quad du = \sum_j \varepsilon_j dp_j + \sum_j d\varepsilon_j p_j \]

b. Boltzmann: \[ p_j = \frac{1}{Z} \frac{e^{-\varepsilon_j/k_BT}}{Z} \]

\[ \Rightarrow \quad \ln p_j = -\frac{\varepsilon_j}{k_BT} - \ln Z \]

\[ \varepsilon_j = -k_BT(\ln p_j + \ln Z) \] ③
c. Entropy of a canonical distribution:

\[ S = k_B \left( -\sum p_j \ln p_j \right) \]

\[ \Rightarrow \quad ds = -k_B \sum p_j \ln p_j - k_B \Sigma dp_j \]

\[ \Rightarrow \quad ds = -k_B \Sigma dp_j \ln p_j \]

and \[ Tds = -k_BT \Sigma dp_j \ln p_j \] ④

Term 0 of \( du \):

\[ \sum_j \varepsilon_j dp_j = -k_BT \sum (\ln p_j + \ln Z) dp_j \]

\[ = -k_BT \left( \sum \ln p_j dp_j + \sum \ln Z dp_j \right) \]

\[ = lnZ \sum dp_j \]

\[ = 0. \]
\[ \sum_j \varepsilon_j \delta p_j = -k_b T \sum_j \ln p_j \delta p_j \]

But from (4),

\[ \sum_j \varepsilon_j \delta p_j = T \delta S. \]

\[ \Rightarrow \text{Term (4) is } T \delta S. \]

d. \[ d\varepsilon_j = \frac{d\varepsilon_j}{dV} \cdot dV \]

First law:

\[ dU = dT - dW \]

\[ dU = T \delta S - P \delta V \]

Free Energy:

\[ F = U - TS \]

\[ \Rightarrow dF = dU - TdS - SdT \]

Substitute:

\[ dF = TdS - PdV \]

\[ = dU \]

\[ \Rightarrow dF = -PdV - SdT \]

\[ \therefore P = - \left( \frac{\partial F}{\partial V} \right)_T \]

e. \[ F = -k_b T \ln Z. \]

\[ P = - \left( \frac{\partial F}{\partial V} \right)_T = + k_b T \left( \frac{\partial \ln Z}{\partial V} \right)_T \]

\[ = k_b T \frac{\partial Z}{Z \left( \frac{\partial V}{\partial V} \right)_T} \]
\( P = \frac{k_b T}{Z} \sum_j \left( \frac{1}{2} k_b T \Xi_j \frac{\partial E_j}{\partial V} \right) \)

\[ = \frac{k_b T}{Z} \sum_j \Xi_j \left( e^{-\frac{3}{2} \frac{k_b T}{E_j}} \frac{\partial E_j}{\partial V} \right) \]

\[ = \sum_j \Xi_j \frac{e^{-\frac{3}{2} \frac{k_b T}{E_j}}}{Z} \frac{\partial E_j}{\partial V} \]

\[ P = \sum_j p_j \frac{\partial E_j}{\partial V} \]

But since \( d\Xi_j = \frac{\partial E_j}{\partial V} dV \), we can write term (2) as

\[ \sum_j d\Xi_j \otimes p_j = \sum_j \frac{\partial E_j}{\partial V} p_j dV \]

\[ = P dV. \]

\[ f \Rightarrow dV = T dS - P dV. \]

We have recovered this fundamental equation from statistical physics. In particular, we can now interpret a reversible heat source as affecting \( S \) (the population of energy levels) as a work change as a change in energy levels themselves.
STATISTICAL PHYSICS
CLASSWORK 3 ANSWERS.

NUCLEAR ENERGY LEVELS

VIBRATIONAL

ELECTRON ENERGY LEVELS

ROTATIONAL

a. In general, write the partition function as

\[ Z = \sum_j \frac{e^{-\beta E_j}}{\beta} \]

where \( j \) is over all possible energy levels.

Here, \( E = E_{tr} + E_r + E_v + E_e + E_n \)

\[ Z = \frac{\sum e^{-\beta E_{tr}} \cdot \sum e^{-\beta E_r} \cdot \sum e^{-\beta E_v} \cdot \sum e^{-\beta E_e} \cdot \sum e^{-\beta E_n}}{\beta} \]

Each summed over the relevant energy levels,

eg. just translational levels for \( E_{tr} \)

\[ Z = Z_{tr} \cdot Z_{r} \cdot Z_{v} \cdot Z_{e} \cdot Z_{n} \]
b. Rotation.

\[ \varepsilon_j = \frac{j(j+1)\hbar^2}{2I} \quad j = 0, 1, 2, \ldots \]

Degeneracy, \( g_j = 2j + 1 \):

\[ Z = \sum_{j=0}^{\infty} g_j e^{-\beta \varepsilon_j} = \sum_{j=0}^{\infty} (2j+1) e^{-\frac{j(j+1)\hbar^2}{2IT}} \]

Define \( \Theta_r = \frac{h^2}{2IT\hbar^2} \).

\[ \Rightarrow Z_r = \sum_{j=0}^{\infty} (2j+1) e^{-\frac{j(j+1)\Theta_r}{T}} \]

For \( T < \theta_r \), \( j = 0 \) term dominates sum.

\[ \Rightarrow Z_r \approx 1 \quad \Rightarrow \Delta \varepsilon = -\frac{\partial \ln Z}{\partial \beta} = 0. \quad \text{(no energy is rotational modes for } T < \theta_r, \text{ no surprise)} \]

For \( T > \theta_r \),

\[ Z_r = \int_0^{\infty} (2j+1) e^{-\frac{j(j+1)\Theta_r}{T}} \, dj \]

\[ x = j(j+1) \Rightarrow \frac{dx}{dj} = 2j+1 \]

\[ \Rightarrow Z_r = \int_0^{\infty} \left( \frac{2j+1}{2\theta_r} \right) e^{-\frac{2j+1}{T}} \, dj \]

\[ = \int_0^{\infty} e^{-\frac{2j+1}{T}} \frac{dx}{2j+1} = \frac{T}{\theta_r} \]

\[ \Rightarrow Z_r = \frac{2I}{\theta_r \hbar^2} \quad \text{for } T > \theta_r \]

\[ \langle \varepsilon \rangle = -\left( \frac{\partial \ln Z}{\partial \beta} \right)_{\varepsilon_N} = -\frac{2}{\beta} \left( -\ln \beta + \ln \frac{2I}{\hbar^2} \right)_{\varepsilon_N} = \frac{1}{\beta} = k_B T \]

Two degrees of freedom: \( = 2 \times \frac{1}{2} k_B T \)
c. Vibrational

\[ Z_v = \frac{e^{-\frac{\beta k_v}{2}}}{1 - e^{-\beta k_v}} \]

\[ \Theta_v = \frac{k_v}{k_B} \]

\[ <\xi> = -\left( \frac{\partial \ln Z}{\partial \beta} \right)_{v, T} = \frac{1}{2} k_v + \frac{k_v}{\exp(\frac{\Theta_v}{T}) - 1} \]

\[ = \frac{1}{2} k_v + \frac{k_B \Theta_v}{\exp(\frac{\Theta_v}{T}) - 1} \]

when \( T \ll \Theta_v \), \( <\xi> = \frac{1}{2} k_v \).

\( T \gg \Theta_v \), \( <\xi> = k_B T \) (not proved here, students can look this from notes).

d. H atom ionisation energy = 13.6 eV

\[ \varepsilon_{\text{ion}} = 13.6 \times 1.6 \times 10^{-19} \]

\[ \Rightarrow T_{\text{ionisation}} = \frac{\varepsilon_{\text{ion}}}{k_B} \approx 1.38 \times 10^{-23} \]

\[ = 160,000 K \]

For, for d don't room temperature!

Electrons energy levels have much more energy than \( k_B T \) at room temperature: electrons sit in the lowest electron density levels that they can.

\[ Z = 0 \text{ or } e^{-\beta k_v} \text{ (least energy)} \]
d. \( Z_n = y^n \) (easy...)

e. \[ Z = Z_{tr} \cdot Z_{int} \]

Note: all internal degrees of freedom do not depend on interaction with surroundings, unlike translational.

Sectin 6.3 of notes,

\[ Z_{tr} = V \cdot \left( \frac{\left(2\pi \text{m} \text{k}_B T\right)}{h^2} \right)^{3/2} \]

\[ m = \text{mass of molecule} \]

Note: no degeneracy here, that's all wrapped up in \( Z_{int} \).

\[ Z_{total} = Z_{tr} \cdot Z_{int} \]

\[ = \frac{Z_{tr}^{N} \cdot Z_{int}^{N}}{N!} \]

\[ = \frac{1}{N!} \left( \frac{\left(2\pi \text{m} \text{k}_B T\right)}{h^2} \right)^{3N/2} \cdot V^N \cdot Z_{int}^{N} \]

Take the log,

\[ \ln Z = N \ln V + \frac{3N}{2} \ln \text{k}_B T + \frac{3N}{2} \ln \frac{2\pi \text{m}}{h^2} + N \ln Z_{int} - N \ln N + N \]

Stirling:

\[ N! = N^{N+1} \]

\[ \ln Z = N \left( \ln V + \frac{3}{2} \ln \text{k}_B T + \frac{3}{2} \ln \frac{2\pi \text{m}}{h^2} + \ln Z_{int} - 1 \right) - 1 \]
So,

\[ U = k_b T^2 \left( \frac{\partial \ln Z}{\partial T} \right)_{V,N} = \frac{3}{2} N k_b T + N k_b T^2 \left( \frac{\partial \ln Z_{inv}}{\partial T} \right)_{V,N} \]

- since all other terms are independent of \( T \).

\[ C_V = \frac{\partial U}{\partial T} \]

; molar means \( N = N_A \n\)

\( \text{Note, } R = N A k_b \).

\[ C_V = \frac{3}{2} R + \left< \text{Contribution from internal degrees of freedom} \right> \]

- We found that rotation contributes 0 for \( T << \Theta_r \) and it contributes \( k_b \) per particle for \( T >> \Theta_r \), since \( \Theta_r < k_b T \).

- For vibration, zero below \( \Theta_v \) and \( k_b \) per particle above \( \Theta_v \).

- Electrons and nuclei do not contribute.

So,

\[ C_V \]

![Graph showing different regions of temperature with \( \Theta_r \) and \( \Theta_v \) as critical points.]

- boiling point not defined below this.
- Room temperature.

T.