

## 3.4: Particle Model of Thermal Energy

### Overview

In the previous section we modeled the macroscopic definition of bond energy from Chapter 1 with the microscopic perspective of neutral subatomic particles interacting with a pair-wise potential. In this section we will attempt to make the same connection for thermal energy. In Chapter 1 for pure substances in the temperature range where the Three-Phase Model is valid we said that the total energy of a system is given by:

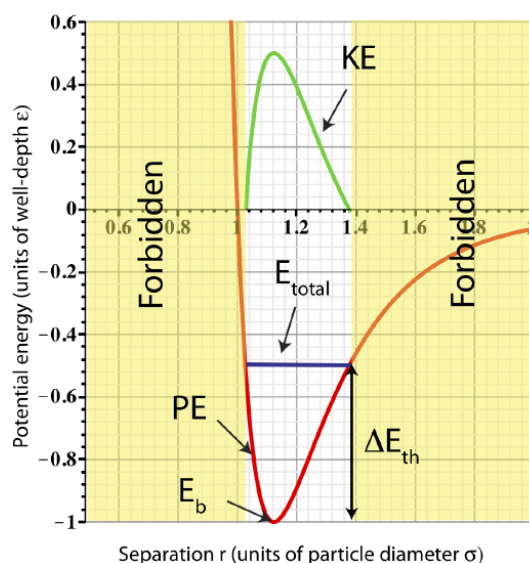
$$E_{tot} = E_b + E_{th} \quad (3.4.1)$$

In the microscopic description of particles interacting with the Lennard-Jones potential the total energy of a system is:

$$E_{tot} = PE_{tot} + KE_{tot} \quad (3.4.2)$$

The subscript "tot" refers to the sum of kinetic and potential energies over all particles. Although, we will focus on just two particles for now, for generality, we add the "tot" subscript so the equations can be applied to many-particles systems, as well. In the previous section we said that macroscopic bond energy can be modeled as the sum of pair-wise *potential energies* between all pairs at their equilibrium configurations (at zero temperature). Your instinct might tell you that thermal energy should be represented in terms of the sum over all the *kinetic energies* of the particles. But careful! If we add some energy to the two-particle system without breaking the bond, the bond energy does not change, so only thermal energy changes. And as we discussed in Section 3.2, when energy is added to the system the particles begin to vibrate about equilibrium. As energy is added to the system increasing thermal energy only, the range of fluctuations increasing, which increases both the average potential and kinetic energy, as can be viewed on the figure below.

Figure 3.5.1: Total Energy in a two-particle system.



Thus, thermal energy is related to potential energy, as well as kinetic. When energy is added, it is not possible to increase kinetic energy without increasing potential energy. As in the spring-mass system when you add potential energy by stretching the spring further, you will also increase the kinetic energy as the spring will oscillate faster on average. In Section 2.6 we discussed that averaged over time the kinetic and potential energies are the same for a spring-mass system, and as a result half of the total energy. Since the Lennard-Jones potential mimics the spring-mass potential at least for small oscillations, we will assume that this interaction when averaged over time will also result in  $KE_{avg} = PE_{avg}$ . When energy is added without breaking bonds all the energy goes into thermal energy which is equally split between kinetic and potential energy:

$$KE_{tot} = \frac{E_{th}}{2} \quad (3.4.3)$$

The potential energy that contributes to the other half of thermal energy has to do with the random vibrations, but there is also the part of potential energy that is equal to bond energy at zero temperature before energy was added:

$$PE_{tot} = \frac{E_{th}}{2} + E_b \quad (3.4.4)$$

To check the validity of these equations add them together to get:

$$KE_{tot} + PE_{tot} = E_{th} + E_b \quad (3.4.5)$$

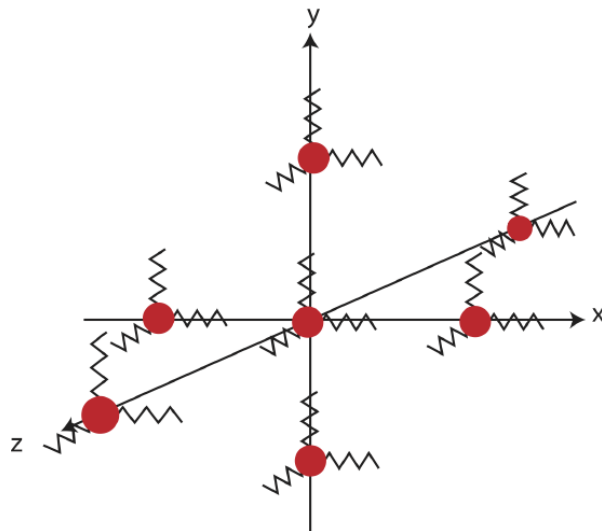
which is precisely the two definitions of total energy given in Equations 3.4.1 and 3.4.2, making the connection between the microscopic and the macroscopic descriptions of total energy.

We saw here that as thermal energy increases the particles start to vibrate about their equilibrium. Thus, thermal energy has to do with the random fluctuations of the particles, while bond energy has to do with their equilibrium configurations. We also discussed the idea of added energy being split evenly between kinetic and potential energies, which will bring us to the idea of *Equipartition of Energy* below.

### Particle Model of Thermal Energy

In the *Particle Model of Thermal Energy* we describe thermal energy of a macroscopic solid or liquid in terms of random fluctuations of subatomic particles which vibrate in the three spatial dimensions. Since most vibrating systems can be described by a spring like potential, we will model these oscillating particles as masses held in place by three perpendicular springs, one for each independent spatial dimension, as depicted in the figure below.

**Figure 3.5.1: Model of thermal energy with particles attached to springs.**



In order to make sense of how thermal energy can be formulated from these random fluctuations, we would like to know how many ways does each of these particles can “have energy” and how is the total energy distributed among these different “ways”? To answer this within the constraints of our model, we start with the fact that a spring-mass system has a kinetic and a potential energy. Because of the randomness or disorder of thermal motions of the microscopic spring-masses in all three spatial directions, it is plausible that on average, each spring would have the same average KE and PE, as would any other spring. The potential and kinetic energies that are associated with those oscillations can *each* be divided into three independent terms, each one corresponding to one of the three independent spatial dimensions. Therefore, *each* particle in a liquid or solid has *at least* these *six* independent ways it can “have energy”.

The important point to remember here, is that regardless of the actual kind of chemical bonding (types of bonds and the geometrical configuration of the bonds) the thermal energy due to the oscillation of the atoms or molecules (treated as rigid particles) is modeled as if they are connected by three independent springs, corresponding to the three independent spatial dimensions in a 3-D universe.

Unbound atoms in the gas phase have other ways to have energy, they can move around freely in space. If the gas is made up of molecules, the individual molecules can also rotate and vibrate. There is a name, or label, for “way to have energy”, which we call a *mode*, also sometimes referred to as a *degree of freedom*.

## Equipartition of Energy

When we discussed a two-particle system, we argued that it is reasonable to assume that half of the thermal energy goes to kinetic and the other half to potential when averaged over time. From the particle model perspective when a macroscopic system reaches thermal equilibrium the energy associated with random fluctuations (the motions of particles about their equilibrium positions in a solid or liquid or their random motions when in the gas phase) is *uniformly distributed throughout the entire sample*. That is, there will be about as much energy associated with the random energies of a small piece of the sample as in any other same size small piece. This is known as *Equipartition of Energy*. It is similar to what we would say about temperature, if we wait for a sufficiently long time, the temperature will become uniform throughout the sample. There would seem to be a direct connection between temperature and the disordered random motion associated with thermal energy.

Using tools of statistical mechanics (which is beyond the scope of this course) it can be shown that each type of energy that a substance can have, or each *mode*, has this amount of thermal energy:

$$E_{\text{thermal}}(\text{per mode}) = \frac{1}{2}k_B T \quad (3.4.6)$$

where  $k_B = 1.38 \times 10^{-23} \text{ J/K}$  is the *Boltzmann constant* and  $T$  is temperature. This expression provides a connection between a macroscopic concept of *temperature* and a microscopic idea of a *mode*. In words the above equation means that *temperature is a measure of the average energy in an active mode when the sample is in thermal equilibrium*. To calculate the total thermal energy, we need to multiple the  $\frac{1}{2}k_B T$  factor for the thermal energy per mode by the total number of modes in our sample. The total number of modes is the total number of particles  $N$  times the number of modes per particle. Thus, total thermal energy can be written as:

$$E_{\text{thermal}} = (\# \text{ modes per particle}) \times N \times \frac{1}{2}k_B T \quad (3.4.7)$$

Our next task is to count the number of modes per particle for different types of substances.

### Counting Modes

When we asked how many ways does *each spring* in a solid can have energy, the answer was two, one kinetic and one potential. We will refer to these modes as the *vibrational kinetic energy*,  $KE_{\text{vib}}$ , and *vibrational potential energy*,  $PE_{\text{vib}}$  modes. To answer how many ways does *each particle* in a solid have to have energy, we saw that there are three springs and two modes per spring, so a solid must be six number of modes, 3  $KE_{\text{vib}}$  modes and 3  $PE_{\text{vib}}$ . *Equipartition of Energy* tells us that each one of these modes will have the same amount of energy of  $\frac{1}{2}k_B T$  at thermal equilibrium. One mole of a solid will have  $6N_A$  number of modes, resulting in a total thermal energy of:

$$E_{\text{thermal}} = 3N_A k_B T \quad (3.4.8)$$

How many modes do different gases have? In a simple *monatomic gas*, composed of single atoms, such as He or Ne gases, *aka* Noble gases, the atoms are no longer interacting with a pair-wise potential since their average separations are  $r \sim 10\sigma$ . Therefore, the atoms cannot be modeled with springs since they are not vibrating around some equilibrium. Rather the atoms are moving around freely in three-dimensions. We refer to this type of motion as *translational kinetic energy*,  $KE_{\text{trans}}$ . Since there are three dimensions, each atom in a monatomic gas will have 3 modes. We can find the average speed of a gas particle by considering that *each* of the three  $KE_{\text{trans}}$  modes has  $\frac{1}{2}k_B T$  of thermal energy. Thus:

$$KE_{\text{avg}} = \frac{1}{2}mv_{\text{avg}}^2 = \frac{3}{2}k_B T \quad (3.4.9)$$

In a *diatomic gas*, composed of two-atom molecules, such as  $\text{H}_2$  or  $\text{O}_2$ , there are still no *inter-molecular* (between molecules) interactions, but there are now *intra-molecular* (between the atoms within a molecule) interactions to consider. We can model the bond between the two atoms in a molecule as a spring, allowing the two atoms to vibrate relative to each other. Thus, each molecule will have one vibrational kinetic and potential energy mode. In addition, as for the monatomic gas, the molecule as a whole is free to move in space, since it is not interacting with other molecules. Thus each molecule has 3 translational kinetic energy modes. Another way this molecule can have kinetic energy is through rotations. The figure below depicts all the possible *rotational modes* of a diatomic molecule. The energy associate with rotations is known as *rotational kinetic energy*,  $KE_{\text{rot}}$ . For a diatomic molecule only two rotational modes are energetically allowed (for quantum mechanical reasons we will not address here). As shown in the figure these are rotations about the y- and z- axes. One way to think about this is that only rotations that change the orientation of the molecule or are not symmetric, are energetically allowed. Thus, since rotating the molecule about the x- axis is symmetric, this rotation is not allowed. For a diatomic gas we have found a total of 7 modes: 3  $KE_{\text{trans}}$ , 2  $KE_{\text{rot}}$ , 1  $KE_{\text{vib}}$ , and 1  $PE_{\text{vib}}$ .



Type of Substance	Translational Modes	Rotational Modes	Vibrational Modes	Total Modes per particle
Solid	0	0	6	6
Monatomic Gas	3	0	0	3
Linear Polyatomic Gas (N atoms)	3	2	6N-10	6N-5
Non-linear Polyatomic Gas (N atoms)	3	3	6N-12	6N-6

Sometimes, however, some of the modes do not “get excited” due to the quantization of energy levels. At low temperatures, the quantum splitting between energy levels is larger than thermal energy, and the mode cannot be activated. When this happens, we say that mode is *frozen out*. *Frozen modes* cannot share thermal energy among other modes. *Active modes* are the only ones that share the thermal energy equally among themselves. Rotational modes typically have lower energy than vibrational modes. Thus, vibrational modes are frozen out for typical temperatures, but rotational modes can also become inactive when the temperature is low enough. Translational modes are always active, as long as the temperature is above zero Kelvin.

### Example 3.4.1

1) You perform various experiments to determine properties of an unknown substance. In one experiment, you place 10 moles of a solid and 12 moles of the unknown substance in separate insulated and sealed containers. You find that when you add the same amount of energy to each container, you measure the same temperature change. Assume there are no phase changes for either substance. Determine whether the unknown substance is a solid, monatomic gas, diatomic gas with frozen vibrational modes, or a diatomic gas with active vibrational modes.

2) In another experiment you combine 2 moles of a solid with 3 moles of a diatomic gas with vibrational modes frozen in an insulated container. The two substances are initially at different temperatures. As the two substances reach thermal equilibrium, which one will have a larger magnitude of a temperature change?

#### Solution

1) In the Particle Model of Thermal Energy the change in thermal energy is given as:

$$\Delta E_{\text{thermal}} = (\# \text{ modes per particle}) \times N \times \frac{1}{2} k_B \Delta T$$

Since  $\Delta E_{\text{thermal}}$  is the same for the same  $\Delta T$  for both substances, the total number of modes must be the same for both substances. The total number of modes is the number of particles times the number of modes per particle, so for the solid we get:

$$\text{total \# modes} = 10N_A \times 6 = 60N_A$$

For the unknown substance:

$$\text{total \# modes} = 60N_A = 12N_A (\# \text{ modes per particle})$$

resulting in (# modes per particle) = 5, which is true for a diatomic gas with frozen vibrational modes.

2) Since the two substances are a closed system,  $\Delta E_{\text{thermal}}$  gained by one substance must equal be  $\Delta E_{\text{thermal}}$  lost by the other:

$$(\text{total \# modes of solid}) |\Delta T_{\text{solid}}| = (\text{total \# modes of gas}) |\Delta T_{\text{gas}}|$$

From equation above, the substance with less total # of modes will have a larger temperature change. The solid has  $2N_A \times 6 = 12N_A$  total number of modes, and the diatomic gas with vibrational modes frozen out has  $3N_A \times 5 = 15N_A$  total number of modes. Thus, the solid will have a larger temperature change.

## Heat Capacity at Constant Volume

Let us now make the connection between the definition of macroscopic thermal energy from Chapter 1 and the microscopic description presented here. Specifically, we would like to develop an understanding of heat capacity from Chapter 1 in terms of microscopic parameters. But we need to be careful that we are actually comparing the same things. We know that if a force acts through a distance, work will be done by one physical object on another. When we make a heat capacity measurement, we do not want the sample doing work on the atmosphere or the container it is in. Therefore, we specify that the sample be kept at constant volume during the heat capacity measurement. The important point here is that we have a way to directly measure the change in the thermal energy by measuring the heat capacity of a sample at constant volume, ensuring all the heat we put into the sample goes to changing its thermal energy and not doing some work by expanding the container or pushing against the air in the room. From the Energy-Interaction Model when no work is being done and only temperature is changing we have  $\Delta E_{tot} = \Delta E_{th} = Q$ . When the change in thermal energy is due solely to the addition or removal of energy as heat, the constant volume heat capacity, designated with subscript "v",  $C_V$ , is given by the rate of change of thermal energy with respect to temperature. This is precisely how we defined thermal energy in Equation 1.2.6 in Chapter 1:

$$\Delta E_{thermal} = C_V \Delta T \quad (3.4.11)$$

except now we add the "V" subscript for accuracy. The expression above is the macroscopic definition of thermal energy at constant volume. Let us compare the above equation with Equation 3.4.7 described in the Particle Model of Thermal Energy. Setting the two equations equal to each other, using the gas constant  $R = N_A k_B = 8.314 \frac{J}{Kmol}$ , and solving for molar heat capacity  $c_{v,mol}$  ( $C_V = c_{v,mol}$  for one mole or  $N_A$  number of particles), we get:

$$c_{v,mol} = \frac{R}{2} (\# \text{ modes per particle}) \quad (3.4.12)$$

We have simple expression above that connects the idea of heat capacity that can be experimentally measured in a lab using macroscopic substances with the microscopic idea of each particle in a substance having an energy mode. We will check the validity of this model next, when we look at some data patterns.

### Example 3.4.1

UC Davis scientists construct the following one-dimensional solid structure from their newly discovered atoms, Aggieum (Ai) and Cyclerium (Cy):



The total number of atoms is  $4N_A$ . The double lines represent strong Ai-Cy bonds, where the single lines are weaker Ai-Cy-Ai-Cy bonds. Each particle is free to move in one-dimension only.

- Calculate the heat capacity  $C_V$  for the substance in the diagram.
- You add enough energy to break all weaker bonds. The resulting gas particles are free to move in three-dimensions. Calculate the heat capacity  $C_V$  for this substance assuming all modes are active.
- You add some more energy, and notice that at  $T=500K$  all of the stronger bonds are broken as well. If the mass of Ai is nine times the mass of Cy, calculate the ratio of their speeds at  $T=500K$ .
- You take two moles of the substance in part a) and one mole of the substance in part b) and place them together in an insulated container. Compare the magnitudes of the changes in thermal energy of the two substances as they come to thermal equilibrium. Assume there is no change in bond energy in the interval you are analyzing.

### Solution

a) Since each atom in this solid can only move in one-dimension, there are 2 modes per atom, one PE and one KE. Heat capacity:

$$C_v = nc_{v,mol} = 4 \times (\# \text{ modes per particle}) \times \frac{R}{2} = 33.26 J/K$$

b) After the weak bonds are broken the AiCy molecules are no longer interacting, so we have a diatomic gas. If all modes are active, there are 7 modes per molecule. Since there are  $4N_A$  total atoms, there will be  $2N_A$  AiCy molecules. Heat capacity:

$$C_v = n c_{v,mol} = 2 \times 7 \times \frac{R}{2} = 58.2 J/K$$

c) Ai and Cy atoms are at the same temperature, thus they'll have the same  $KE = \frac{3}{2} k_B T = \frac{1}{2} m v^2$ . Setting the two kinetic energies equal to each other:

$$\frac{1}{2} m_{Ai} v_{Ai}^2 = \frac{1}{2} m_{Cy} v_{Cy}^2$$

$$\frac{v_{Cy}^2}{v_{Ai}^2} = \frac{m_{Ai}}{m_{Cy}} = 9$$

$$\frac{v_{Cy}}{v_{Ai}} = 3$$

Thus, Cy atoms are on average moving three times faster than Ai atoms.

d) Only the idea of energy conservation is needed to answer this question. They are in an insulated container:

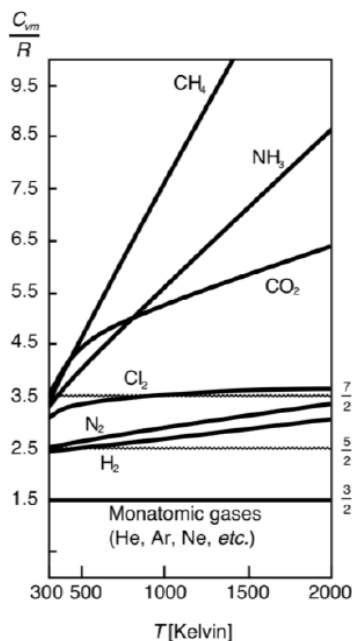
$$\Delta E_{th,a} + \Delta E_{th,b} = 0$$

Thus, both will have the same magnitude of change in thermal energy.

## Data Patterns

The figure below shows the constant volume molar heat capacity, scaled with gas constant, for several gases from room temperature up to several thousand kelvin. Since  $c_{v,mol}/R = (\# \text{ modes per particle})/2$ , the plot is showing us how the number of modes per particle changes with temperature. The monatomic gases have the lowest molar constant volume heat capacity of  $\frac{3}{2}R$ , and the values are independent of temperature. Diatomic gases seem to have higher values starting at about  $\frac{5}{2}R$ , while polyatomic gases have significantly larger values, but also a much more pronounced temperature dependence. This data tells us that not all modes are active at all temperature. As we previously discussed at lower temperature some modes get *frozen out* when there is not enough energy to overcome the quantum energy gap to excite a particular mode. For example, we see that around room temperature diatomic molecules have 5 modes, instead of the possible 7 modes, implying that the two vibrational modes are inactive. This data shows an average over one mole of particles, this is why the number of modes changes smoothly (rather than by integer count) as modes become activated in an increasing number of particles as temperature increases.

**Figure 3.5.4: Heat Capacity as a function for temperature for various gases.**



The table below shows heat capacity patterns that are seen in different gases. Each type of gas, e.g., monatomic, has similar values of specific heats, and the values are ordered from smaller to larger as we go from monatomic to diatomic to triatomic, as implied by Equation 3.4.12. We will analyze in the next chapter why the specific heats of gases measured at constant pressure are greater than at constant volume, as well as the similar difference between  $C_{mp}$  and  $C_{mv}$  for all gases.

**Table 3.2.1: Molar values of both  $C_p$  and  $C_v$  for monatomic, diatomic, and triatomic gases at room temperature.**

gas	$C_{mp}$	$C_{mv}$	$\frac{C_{mv}}{R}$	$C_{mp} - C_{mv}$	$\frac{(C_{mp} - C_{mv})}{R}$
<b>Monatomic</b>					
He	20.79	12.52	1.51	8.27	0.99
Ne	20.79	12.68	1.52	8.11	0.98
Ar	20.79	12.45	1.50	8.34	1.00
Li	20.79	12.45	1.50	8.34	1.00
Xi	20.79	12.52	1.51	8.27	0.99
<b>Diatomic</b>					
N <sub>2</sub>	29.12	20.80	2.50	8.32	1.00
H <sub>2</sub>	28.82	20.44	2.46	8.38	1.01
O <sub>2</sub>	29.37	20.98	2.52	8.39	1.01
CO	29.04	20.74	2.49	8.30	1.00
<b>Triatomic</b>					
CO <sub>2</sub>	36.62	28.17	3.39	8.45	1.02
N <sub>2</sub> O	36.90	28.39	3.41	8.51	1.02
H <sub>2</sub> S	36.12	27.36	3.29	8.76	1.05

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