Specific Heats of Ideal Gases 1

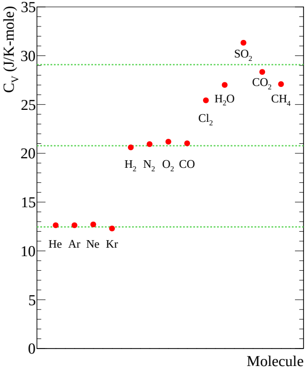
Assume that a pure, ideal gas is made of tiny particles that bounce into each other and the walls of their cubic container of side ℓ. Show the average pressure P exerted by this gas is

$$P = \frac{1}{3}\frac{N}{V}m\overline{v_{total}^2}$$

Use the ideal gas law ($PV = Nk_BT = nRT$)and the conservation of energy ($\Delta E_{int} = C_V \Delta T$) to calculate the specific heat of an ideal gas and show the following.

$$C_V = \frac{3}{2}N_Ak_B = \frac{3}{2}R$$

Is this right?



$$\frac{7}{2}R = \frac{7}{2}N_Ak_B$$

$$\frac{5}{2}R = \frac{5}{2}N_Ak_B$$

$$\frac{3}{2}R = \frac{3}{2}N_Ak_B$$

N - number of particles

k_B - Boltzmann constant

N_A - Avogadro's number

$V = \ell^3$

m - atomic mass

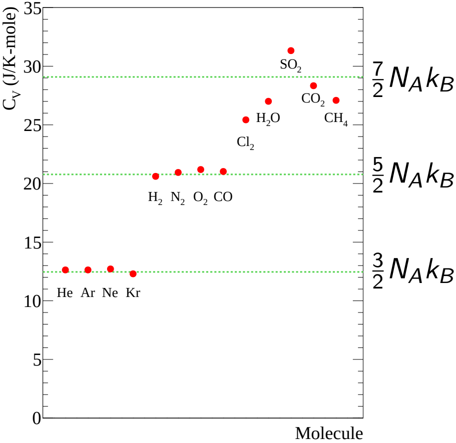
v_{total} - atom's speed

The Results

$$P = \frac{1}{3}\frac{N}{V}m\overline{v_{total}^2} = \frac{2}{3}\frac{N}{V}\langle E_{kin}\rangle$$

$$\langle E_{kin}\rangle = \frac{3}{2}Nk_BT$$

$$C_V = \frac{3}{2}N_Ak_B = \frac{3}{2}R$$



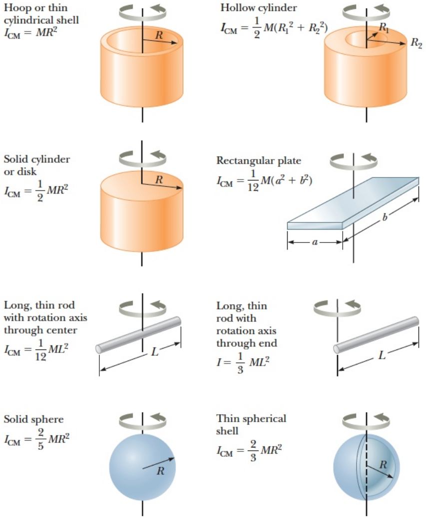
Rotational Kinetic Energy

Classically

$$E_{rot} = \frac{\mathcal{L}^2}{2\mathcal{I}}$$

where

$$\mathcal{I} = \sum m r_i^2 = \int r^2 dm$$



Rotational Kinetic Energy

Classically

$$E_{rot} = \frac{\mathcal{L}^2}{2\mathcal{I}}$$

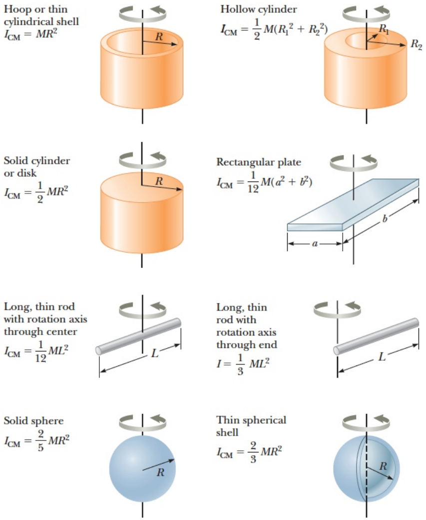
where

$$\mathcal{I} = \sum m r_i^2 = \int r^2 dm$$

Quantum mechanically

$$E_{rot}^{qm} = \ell(\ell+1)\frac{\hbar^2}{2\mathcal{I}}$$

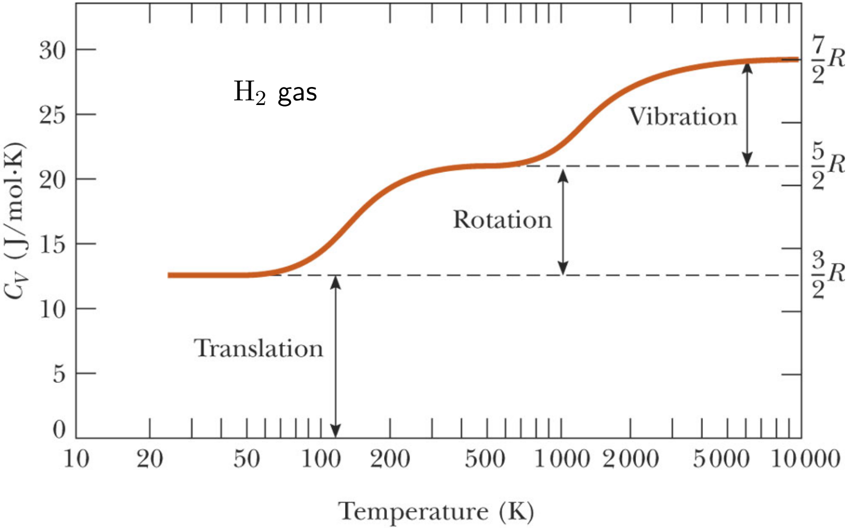
where l is the angular momentum quantum number.



The Kinetic Model of Ideal Gases

1. The gas consists of a large number of small, mobile particles and their average separation is large.
2. The particles obey Newton's Laws and the conservation laws, but their motion can be described statistically.
3. The particles' collisions are elastic.
4. The inter-particle forces are small until they collide.
5. The gas is pure.
6. The gas is in thermal equilibrium with the container walls.

A Hint of Quantum Mechanics



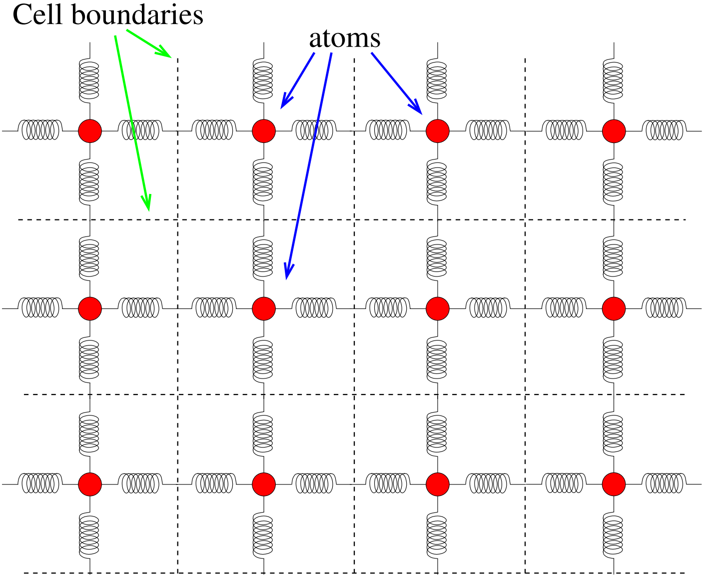
The Specific Heat of Elemental Solids - 2

Solid	Molar Specific Heat (J/K-mole)	Our Results (J/K-mole)
Lead	26.4	22 ± 6
Zinc	25.4	36 ± 14
Aluminum	26.4	24 ± 5
Copper	24.5	23 ± 5
Tin	27.0	52 ± 15
Gold	25.4	
Silver	25.4	
Iron	25.0	

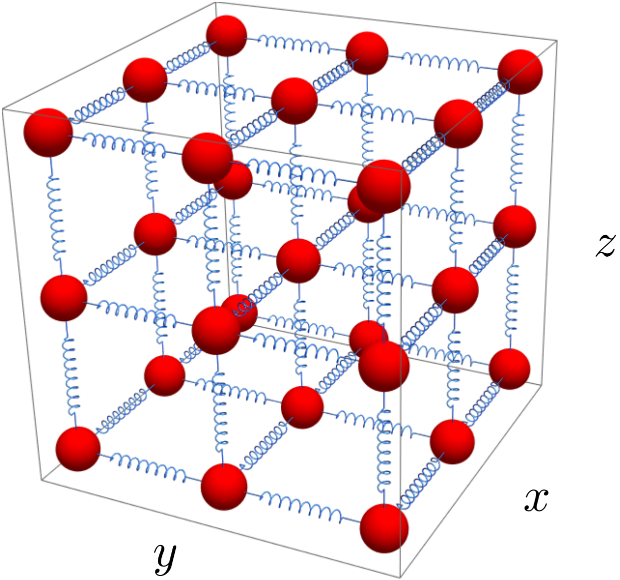
The Specific Heat of Elemental Solids - 2

Solid	Molar Specific Heat (J/K-mole)	Our Results (J/K-mole)	$3R$ (J/K-mole)
Lead	26.4	22 ± 6	24.9434
Zinc	25.4	36 ± 14	24.9434
Aluminum	26.4	24 ± 5	24.9434
Copper	24.5	23 ± 5	24.9434
Tin	27.0	52 ± 15	24.9434
Gold	25.4		24.9434
Silver	25.4		24.9434
Iron	25.0		24.9434

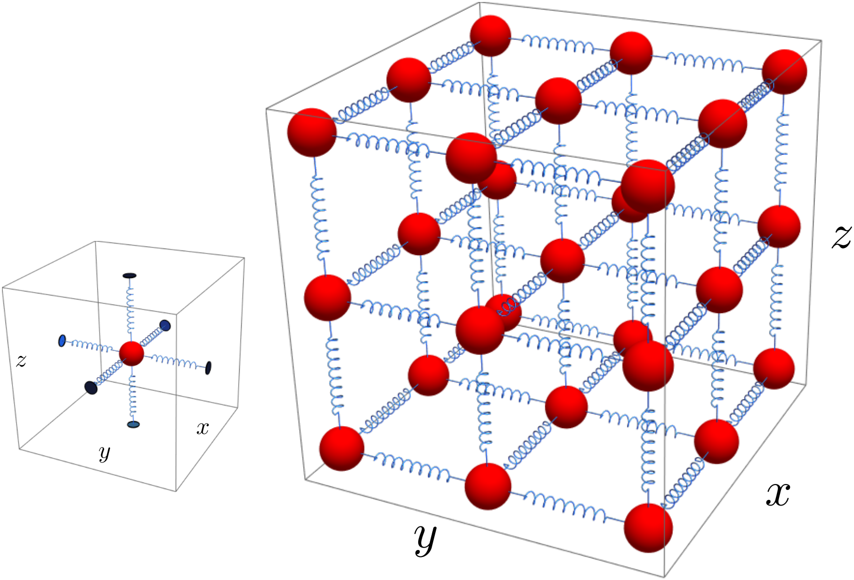
The Einstein Solid



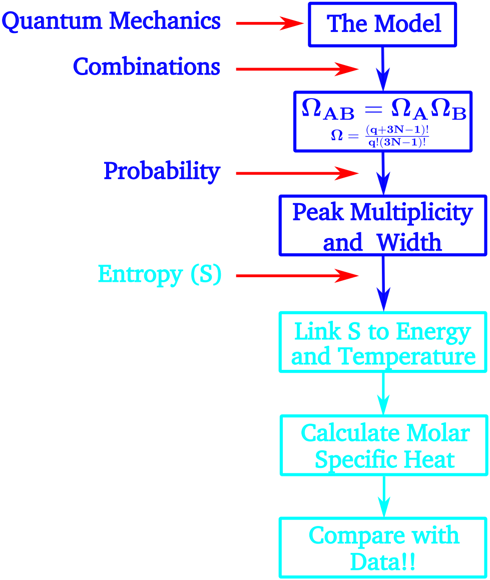
The Einstein Solid



The Einstein Solid



The Plan



Quantum Mechanics

The Model

Combinations

$$\Omega_{AB} = \Omega_A \Omega_B$$

$$\Omega = \frac{(q+3N-1)!}{q!(3N-1)!}$$

Probability

Peak Multiplicity and Width

Entropy (S)

Link S to Energy and Temperature

Calculate Molar Specific Heat

Compare with Data!!

Molar Specific Heat of Elemental Solids

An Einstein solid is made of N, three-dimensional harmonic oscillators containing q quanta of energy.

1. What is the multiplicity of a single Einstein solid?
2. What is the multiplicity of two Einstein solids in thermal contact?
3. How would you determine the most likely microstate of the system?
4. How is entropy related to temperature?
5. How is the energy related to temperature?
6. What is the molar specific heat of an elemental solid?

Solid	Molar Specific Heat (J/K-mole)	Our Results (J/K-mole)
Lead	26.4 ± 0.7	22 ± 6
Zinc	25.4 ± 0.6	36 ± 14
Aluminum	26.4 ± 0.2	24 ± 3
Copper	24.5 ± 0.6	23 ± 5
Tin	27.0 ± 0.6	52 ± 15
Gold	25.4 ± 0.6	
Silver	25.4 ± 0.6	
Iron	25.0 ± 0.6	

Rolling Dice

Rolling Dice

Total	Combinations	No. of combos
2	1-1	1
3	1-2,2-1	2
4	1-3,2-2,3-1	3
5	1-4,2-3,3-2,4-1	4
6	1-5,2-4,3-3,4-2,5-1	5
7	1-6,2-5,3-4,4-3,5-2,6-1	6
8	2-6,3-5,4-4,5-3,6,2	5
9	3-6,4-5,5-4,6-3	4
10	4-6,5-5,6-4	3
11	5-6,6-5	2
12	6-6	1

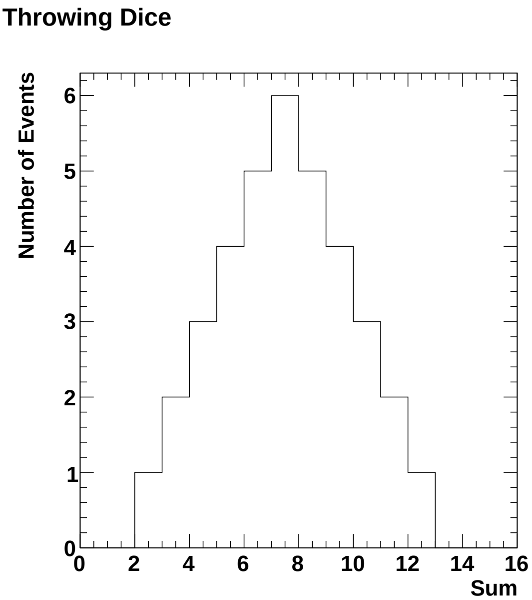
Rolling Dice

Total	Combinations	No. of combos
2	1-1	1
3	1-2,2-1	2
	1-3,2-2,3-1	3
5	1-4,2-3,3-2,4-1	4
6	1-5,2-4,3-3,4-2,5-1	5
7	1-6,2-5,3-4,4-3,5-2,6-1	6
8	2-6,3-5,4-4,5-3,6,2	5
9	3-6,4-5,5-4,6-3	4
10	4-6,5-5,6-4	3
11	5-6,6-5	2
12	6-6	1

macrostate

microstates

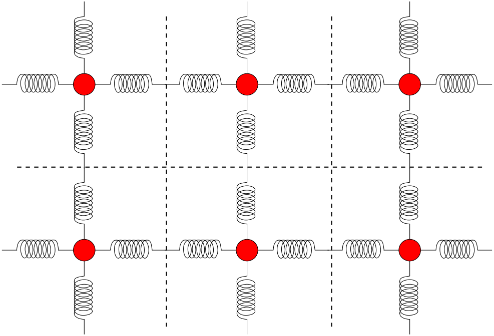
A Probability Distribution



The Entropy of the Einstein Solid

An Einstein solid is made of N, three-dimensional harmonic oscillators containing q quanta of energy as shown below.

1. What is the energy of a single oscillator? of N oscillators?
2. How many microstates Ω exist for a 'system' with $N = 1$ and $q = 3$? for $N = 2$, $q = 2$?
3. What is Ω for any N and q?



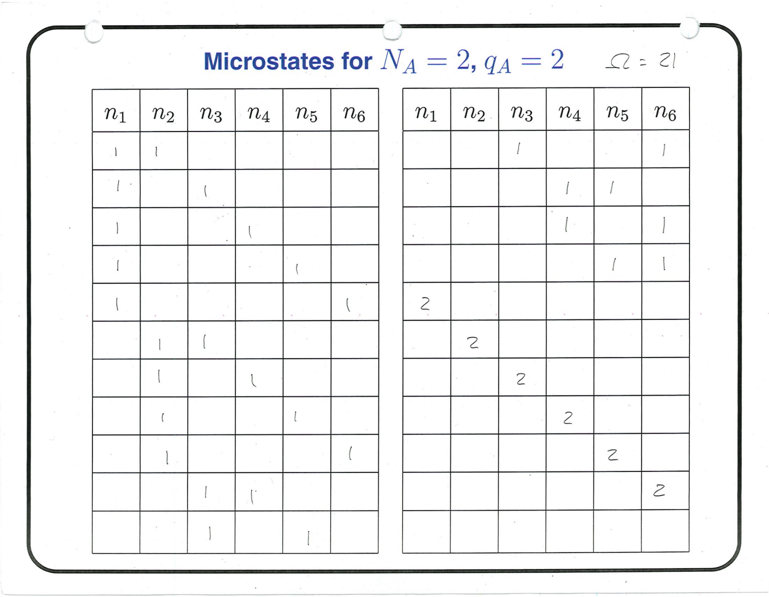
Microstates for $N_A = 2$, $q_A = 2$

19

n_1	n_2	n_3	n_4	n_5	n_6

n_1	n_2	n_3	n_4	n_5	n_6

Microstates for $N_A = 2$, $q_A = 2$



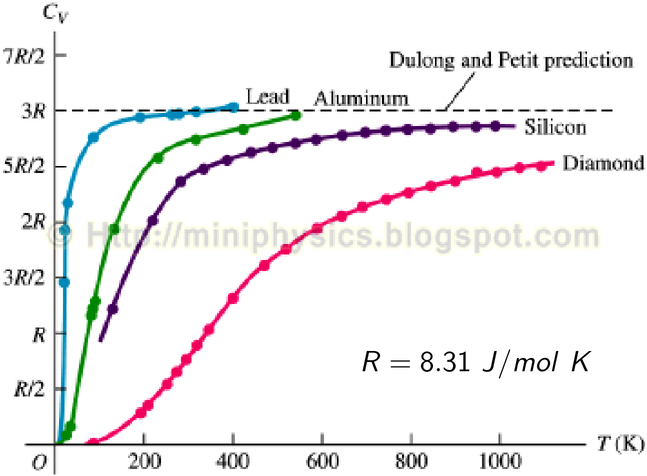
Microstates for $N_A = 2, q_A = 2$

$\Omega = 21$

n_1	n_2	n_3	n_4	n_5	n_6
1	1				
1		1			
1			1		
1				1	
1					1
	1	1			
	1		1		
	1			1	
	1				1
		1	1		
		1		1	

n_1	n_2	n_3	n_4	n_5	n_6
		1			1
			1	1	
			1		1
				1	1
2					
	2				
		2			
			2		
				2	
					2

The Specific Heat of Elemental Solids - 1



$R = 8.31\ J/mol\ K$

Summary So Far

$$E_{int} = (n_x + n_y + n_z)\hbar\omega = \sum_{i=1}^{3N} n_i \hbar\omega \qquad \textit{for N atoms}$$

multiplicity (Ω)	number of microstates
macrostate	configuration of a solid defined by bulk properties like N and E/U.
microstate	one of the configurations of quanta consistent with the macrostate.

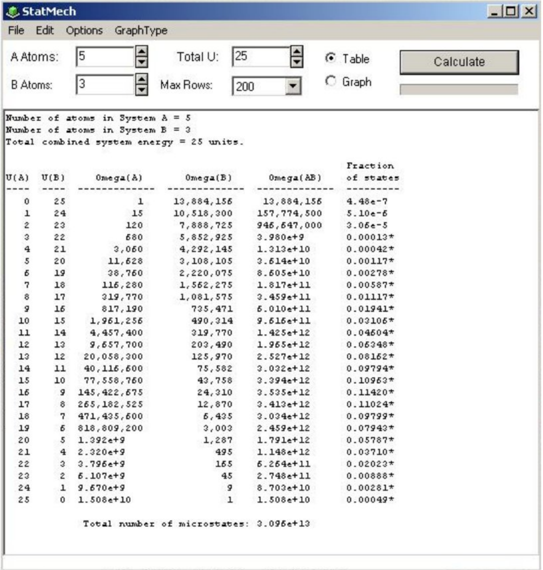
$$\Omega(N_A, q_A) = \frac{(q_A + 3N_A - 1)!}{q_A!(3N_A - 1)!}$$

$\Omega_{AB} = \Omega_A \Omega_B$ *where*
Ω_{AB} - multiplicity of combined state
$\Omega_{A,B}$ - individual multiplicities.

Summary So Far

E_{int} oms

multiplicit	
macrostat	lk proper-
microstate	consistent



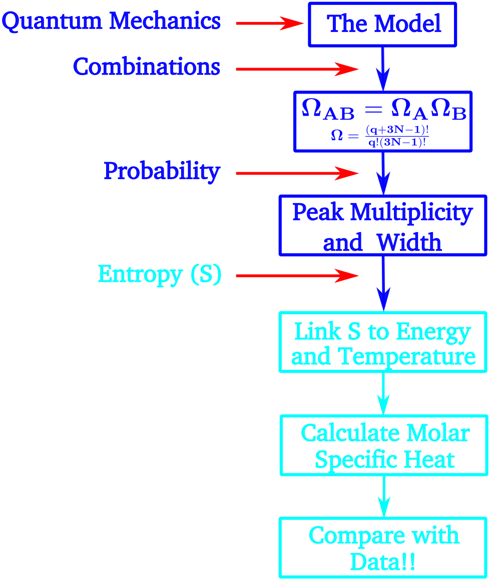
A Atoms: 5
Total U: 25
● Table
B Atoms: 3
Max Rows: 200
○ Graph

```
Number of atoms in System A = 5
Number of atoms in System B = 3
Total combined system energy = 25 units.

                                                         Fraction
U(A)  U(B)     Omega(A)          Omega(B)        Omega(AB)      of states
----  ----  -------------   -------------   -------------   ---------
   0    25              1      13,884,156      13,884,156   4.48e-7
   1    24             15      10,518,300     157,774,500   5.10e-6
   2    23            120       7,888,725     946,647,000   3.06e-5
   3    22            680       5,852,925     3.980e+9      0.00013*
   4    21          3,060       4,292,145     1.313e+10     0.00042*
   5    20         11,628       3,108,105     3.614e+10     0.00117*
   6    19         38,760       2,220,075     8.605e+10     0.00278*
   7    18        116,280       1,562,275     1.817e+11     0.00587*
   8    17        319,770       1,081,575     3.459e+11     0.01117*
   9    16        817,190         735,471     6.010e+11     0.01941*
  10    15      1,961,256         490,314     9.616e+11     0.03106*
  11    14      4,457,400         319,770     1.425e+12     0.04604*
  12    13      9,657,700         203,490     1.965e+12     0.06348*
  13    12     20,058,300         125,970     2.527e+12     0.08162*
  14    11     40,116,600          75,582     3.032e+12     0.09794*
  15    10     77,558,760          43,758     3.394e+12     0.10963*
  16     9    145,422,675          24,310     3.535e+12     0.11420*
  17     8    265,182,525          12,870     3.413e+12     0.11024*
  18     7    471,435,600           6,435     3.034e+12     0.09799*
  19     6    818,809,200           3,003     2.459e+12     0.07943*
  20     5    1.392e+9              1,287     1.791e+12     0.05787*
  21     4    2.320e+9                495     1.148e+12     0.03710*
  22     3    3.796e+9                165     6.264e+11     0.02023*
  23     2    6.107e+9                 45     2.748e+11     0.00888*
  24     1    9.670e+9                  9     8.703e+10     0.00281*
  25     0    1.508e+10                 1     1.508e+10     0.00049*

          Total number of microstates: 3.096e+13
```

Ω_{AB} nbined state

icities.

The Plan



Quantum Mechanics

The Model

Combinations

$$\Omega_{AB} = \Omega_A \Omega_B$$

$$\Omega = \frac{(q+3N-1)!}{q!(3N-1)!}$$

Probability

Peak Multiplicity and Width

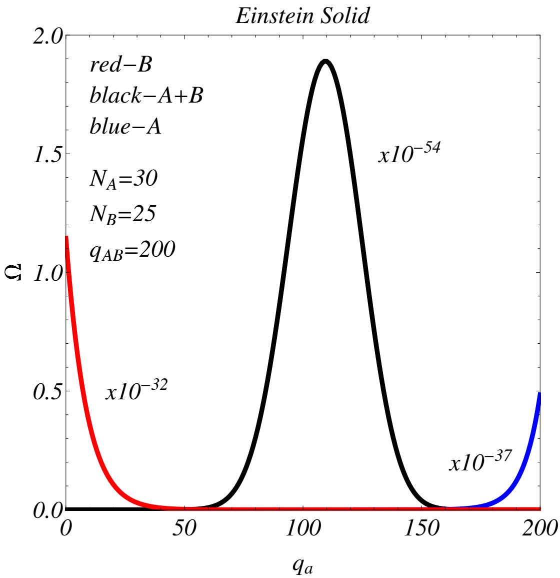
Entropy (S)

Link S to Energy and Temperature

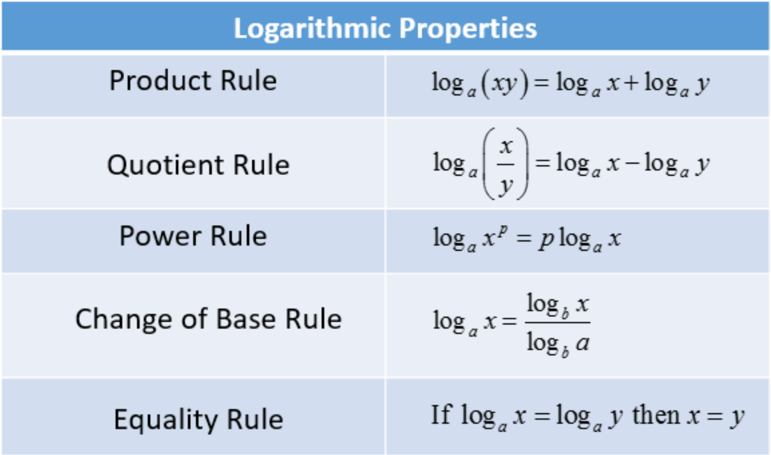
Calculate Molar Specific Heat

Compare with Data!!

Multiplicity and Number of Quanta

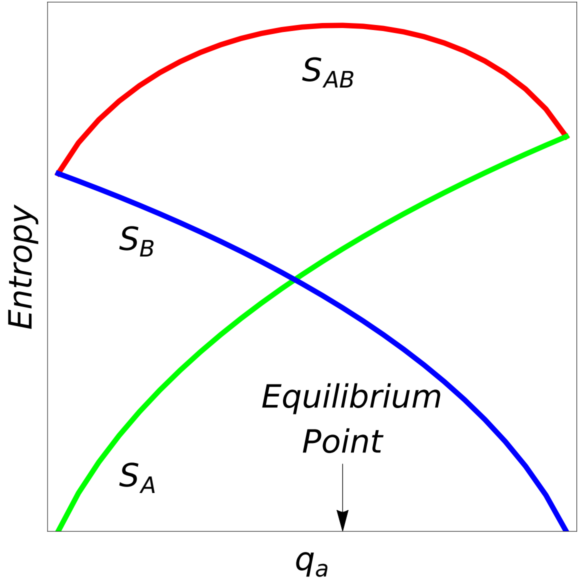


Some Math - Logarithms

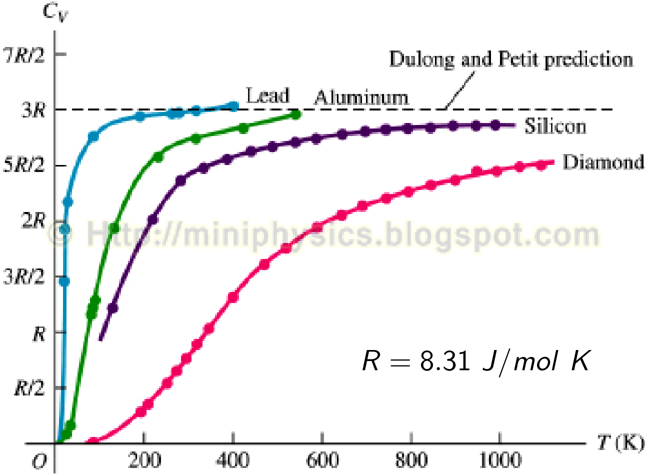


Logarithmic Properties	
Product Rule	$\log_a(xy) = \log_a x + \log_a y$
Quotient Rule	$\log_a\left(\frac{x}{y}\right) = \log_a x - \log_a y$
Power Rule	$\log_a x^p = p\log_a x$
Change of Base Rule	$\log_a x = \frac{\log_b x}{\log_b a}$
Equality Rule	If $\log_a x = \log_a y$ then $x = y$

Entropy of Two Einstein Solids

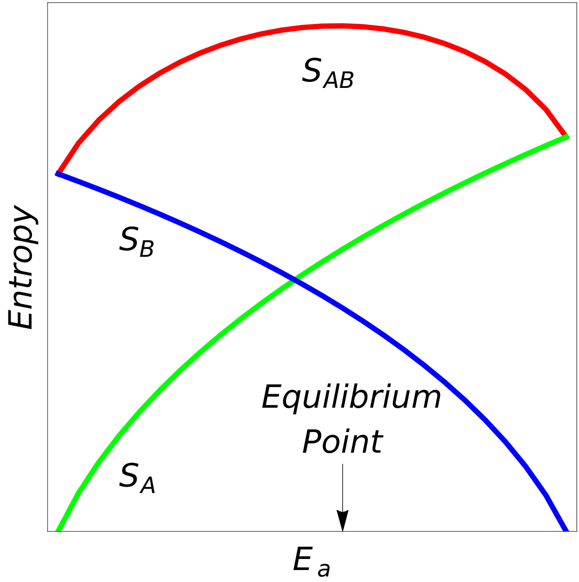


The Specific Heat of Elemental Solids - 1

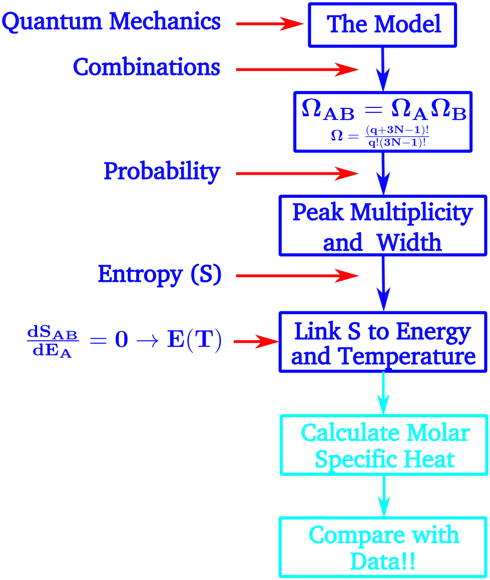


$R = 8.31\ J/mol\ K$

Entropy of Two Einstein Solids in Energy Terms



The Plan



Quantum Mechanics → The Model

Combinations

$\Omega_{AB} = \Omega_A \Omega_B$

$\Omega = \frac{(q+3N-1)!}{q!(3N-1)!}$

Probability

Peak Multiplicity and Width

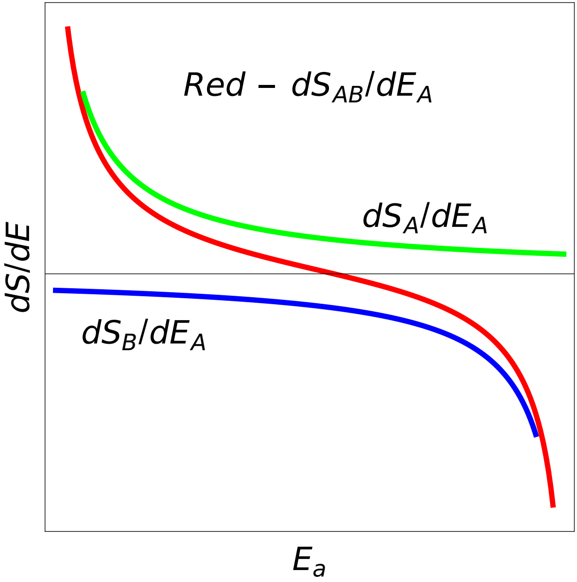
Entropy (S)

$\frac{dS_{AB}}{dE_A} = 0 \rightarrow E(T)$ → Link S to Energy and Temperature

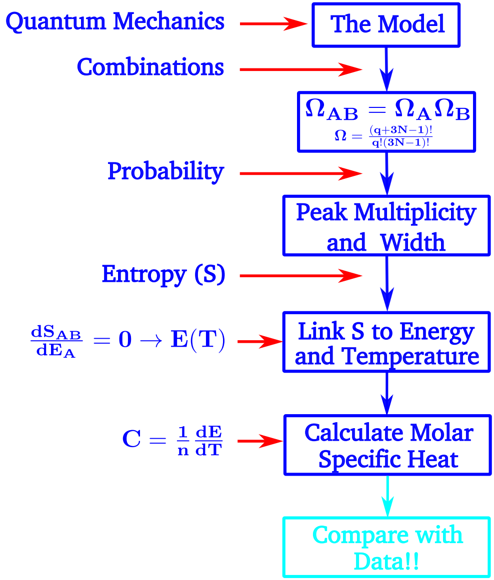
Calculate Molar Specific Heat

Compare with Data!!

Slopes



The Plan



Quantum Mechanics → The Model

Combinations →

$$\Omega_{AB} = \Omega_A \Omega_B$$

$$\Omega = \frac{(q+3N-1)!}{q!(3N-1)!}$$

Probability →

Peak Multiplicity and Width

Entropy (S) →

$\frac{dS_{AB}}{dE_A} = 0 \rightarrow E(T)$ → Link S to Energy and Temperature

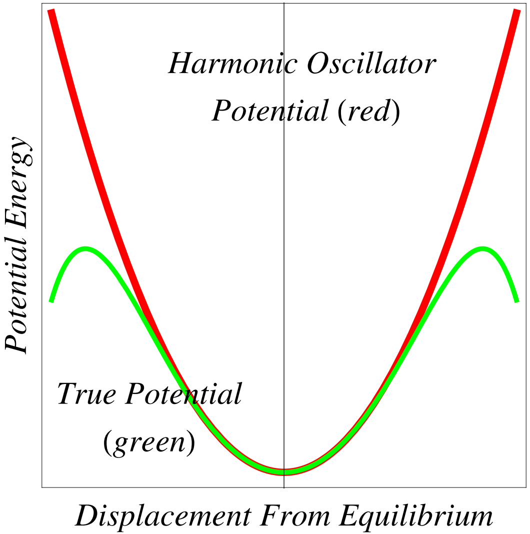
$C = \frac{1}{n}\frac{dE}{dT}$ → Calculate Molar Specific Heat

Compare with Data!!

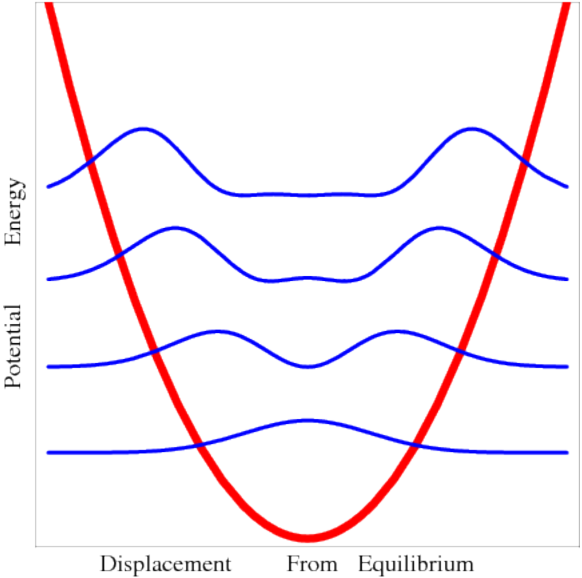
The Specific Heat of Elemental Solids

Solid	Measured Molar Specific Heat (J/K-mole)	Our Results (J/K-mole)	Our Calculation (J/K-mole)
Lead	26.4 ± 0.7	22 ± 8	24.9
Zinc	25.4 ± 0.6	36 ± 14	24.9
Aluminum	26.4 ± 0.2	24 ± 3	24.9
Copper	24.5 ± 0.6	23 ± 5	24.9
Tin	27.0 ± 0.6	52 ± 15	24.9
Gold	25.4 ± 0.6		24.9
Silver	25.4 ± 0.6		24.9
Iron	25.0 ± 0.6		24.9

The Harmonic Oscillator Approximation



Quantum Oscillator



Installing Capstone

1. Go to the website

   `https://www.pasco.com/downloads/capstone`

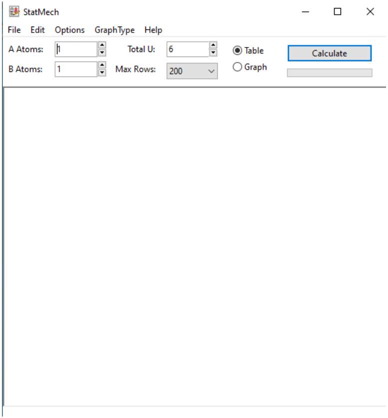
   and select the free trial for your platform (Windows or Mac). The installer will be downloaded to your machine.
2. Launch the installer you just downloaded.
3. Accept defaults.
4. On first launch, enter the license key listed below.

   19F5C-S10o2-4o0m0-ppip3-40qr8-ece1h
5. The capstone files for each lab will be linked to the lab schedule on the course website at the following location.

   `https://facultystaff.richmond.edu/~ggilfoyl/genphys.html`

Installing *statmech.exe*

1. Go to: `http://www.physics.pomona.edu/sixideas/old/sicpr.html`
2. Scroll down to the section entitled "For Use With Unit T:".
3. Scroll down to the paragraph that starts with "statmech 2.7".
4. Scroll down to "Download for:" and right click on "Windows" or "Mac OSX" and save it to your Desktop.
5. On your desktop double click on the folder entitled "statmech.exe.zip". You should see a list of the contents of the folder.
6. Click the "`Extract All`" button and then choose the Desktop (it it's not already set) to place the files.
7. Double click on "*statmech.exe*" and you will now see the contents of the folder with the application.
8. Double click on "*statmech.exe*". You will get a GUI like the one shown here.
9. You're off.



A Atoms: 1

Total U: 6

● Table

○ Graph

B Atoms: 1

Max Rows: 200

Updating *equilib.exe*

1. Go to: `http://www.physics.pomona.edu/sixideas/old/sicpr.html`
2. Scroll down to the section entitled “For Use With Unit T:”.
3. Scroll down to the paragraph that starts with “Equilib 2.1”.
4. Scroll down to “Download for:” and right click on “Windows” and save it to your Desktop.
5. Double click on the folder entitled “Equil.exe.zip”. You should see a list of the contents of the folder.
6. Double click on “*Equilib.exe*”. You should get a GUI telling you the application may depend on other compressed files in the folder. Click the “`Extract All`” button and then choose the Desktop to place the files.
7. Double click on “*Equilib.exe*” and you will now see the contents of the folder with the application.
8. Double click on “*Equilib.exe*”. You will get a GUI worrying about the publisher.
9. Click “`Run`” and you’re off.