Specific Heats of Ideal Gases 1

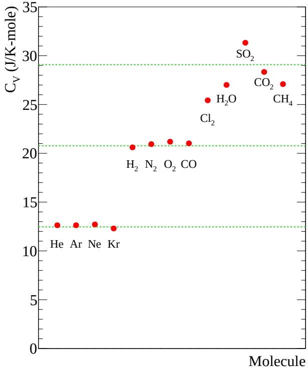
Assume that a pure, ideal gas is made of tiny particles that bounce into each other and the walls of their cubic container of side ℓ. Show the average pressure P exerted by this gas is

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

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.

$$C_V = \frac{3}{2}N_A k_B = \frac{3}{2}R$$

Is this right?



$\frac{7}{2}R = \frac{7}{2}N_A k_B$

$\frac{5}{2}R = \frac{5}{2}N_A k_B$

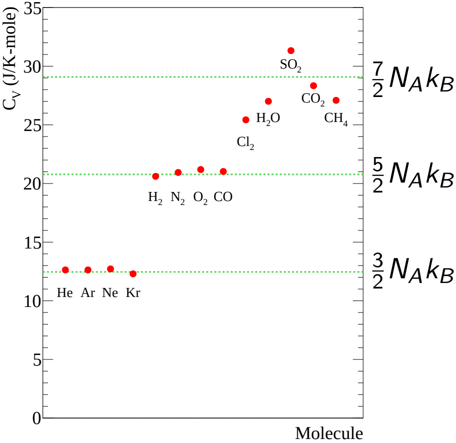
$\frac{3}{2}R = \frac{3}{2}N_A k_B$

N - number of particles	$V = \ell^3$
k_B - Boltzmann constant	m - atomic mass
N_A - Avogadro's number	v_{total} - atom's speed

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

$$\langle E_{kin}\rangle = \frac{3}{2} N k_B T$$

$$C_V = \frac{3}{2} N_A k_B = \frac{3}{2} R$$

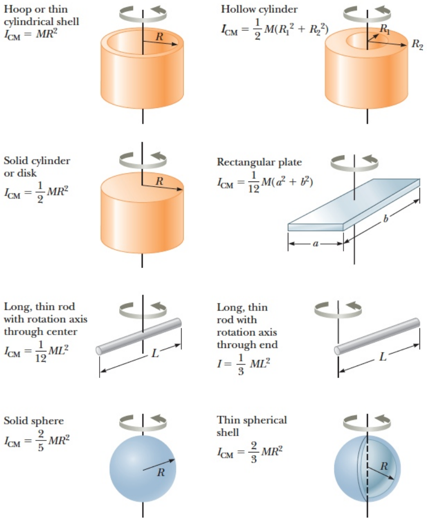


Classically

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

where

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



Classically

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

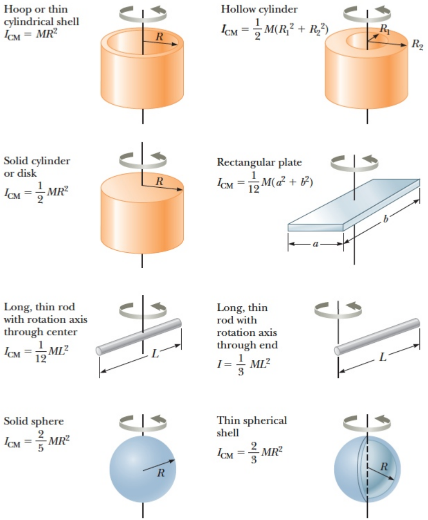
where

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

Quantum mechanically

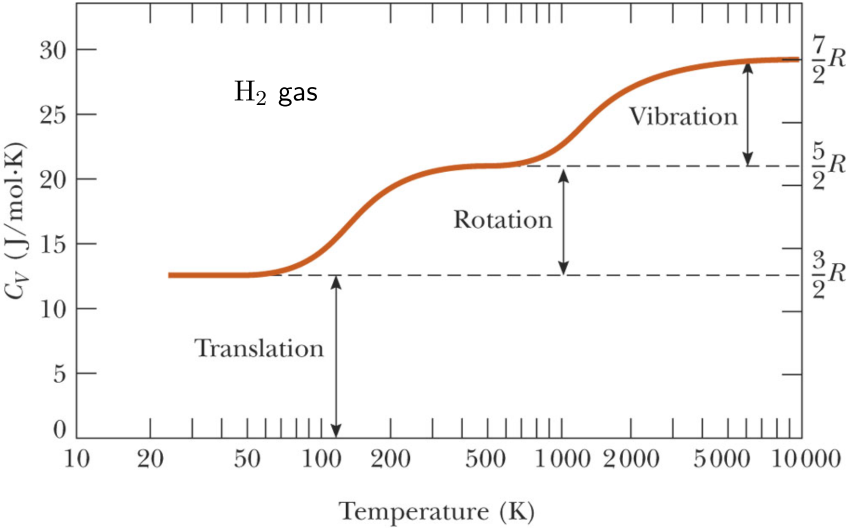
$$E_{rot}^{qm} = \ell(\ell+1)\frac{\hbar^2}{2\mathcal{I}}$$

where l is the angular momentum quantum number.



The Kinetic Model of Ideal Gases 5

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.

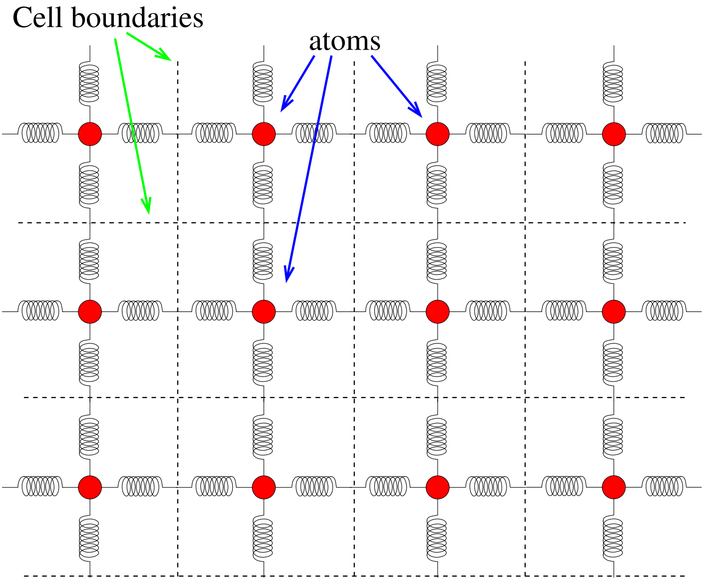


H$_2$ gas
C_V (J/mol·K)
30
25
20
15
10
5
0
10
20
50
100
200
500
1000
2000
5000
10000
Temperature (K)
Translation
Rotation
Vibration
$\frac{7}{2}R$
$\frac{5}{2}R$
$\frac{3}{2}R$

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	21 ± 9
Copper	24.5	25 ± 9
Tin	27.0	64 ± 47
Gold	25.4	
Silver	25.4	
Iron	25.0	

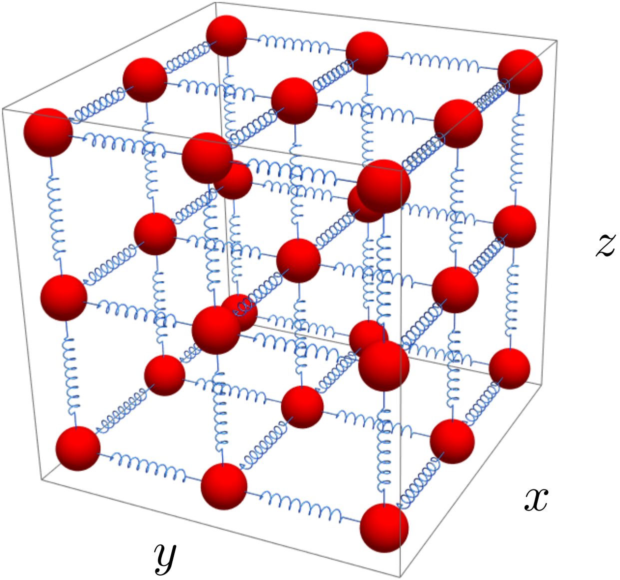
The Specific Heat of Elemental Solids - 2 8

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	21 ± 9	24.9434
Copper	24.5	25 ± 9	24.9434
Tin	27.0	64 ± 47	24.9434
Gold	25.4		24.9434
Silver	25.4		24.9434
Iron	25.0		24.9434

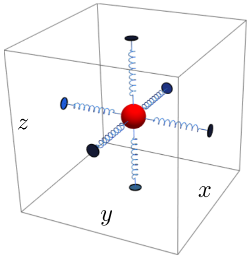


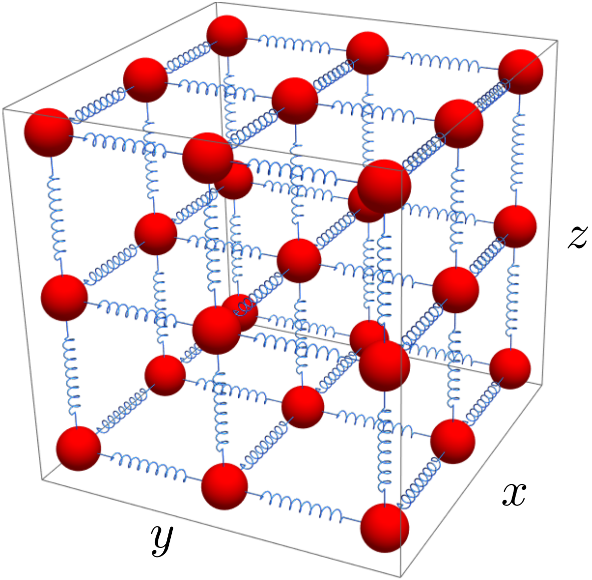
Cell boundaries
atoms

The Einstein Solid



The Einstein Solid 11





$$E_{atom} = n_x\hbar\omega + n_y\hbar\omega + n_z\hbar\omega$$

The n_i are integers and $\hbar$ and ω are constants.

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	21 ± 9
Copper	24.5 ± 0.6	25 ± 9
Tin	27.0 ± 0.6	64 ± 47
Gold	25.4 ± 0.6	
Silver	25.4 ± 0.6	
Iron	25.0 ± 0.6	

Rolling Dice 14

Rolling Dice

15

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

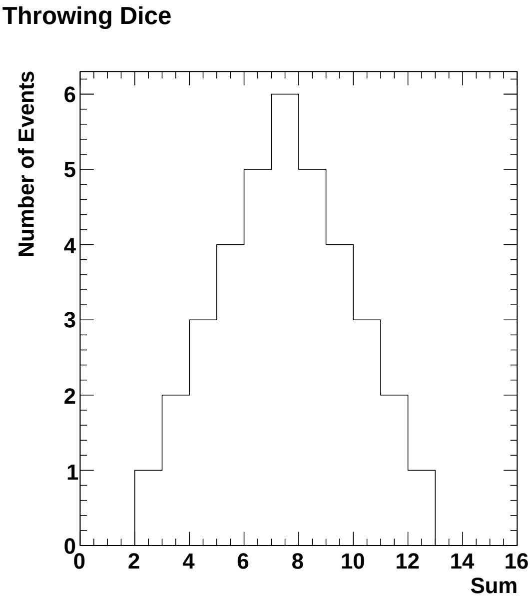
Rolling Dice 16

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 → 6

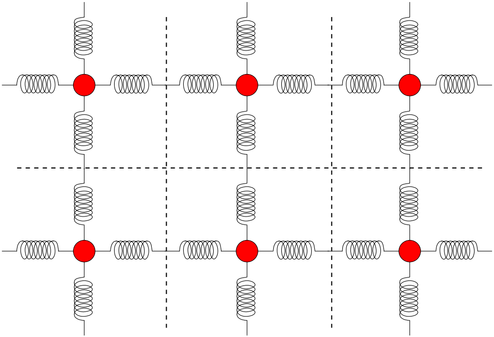
microstates → 1-5,2-4,3-3,4-2,5-1

A Probability Distribution



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 $N_A = 2$, $q_A = 2$ 20

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

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

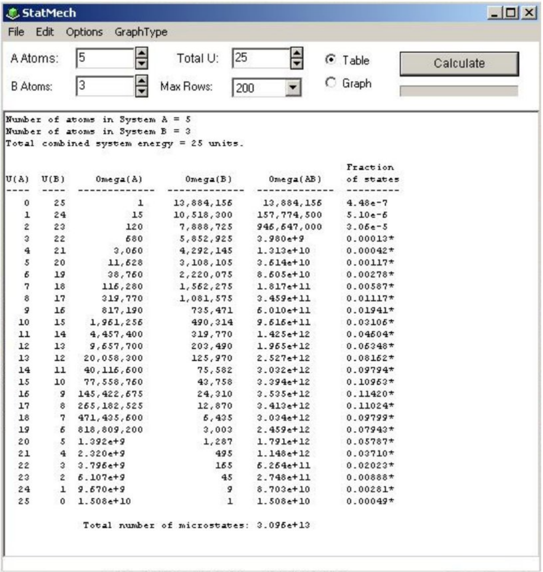
multiplicity (Ω)	number of microstates
macrostate	configuration of a solid defined by bulk properties like N and E/U.
microstate	one of the configurations of quanta consistent with the macrostate.

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

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

E_{int} … oms

multiplicit	
macrostat	lk proper-
microstate	consistent



U(A)	U(B)	Omega(A)	Omega(B)	Omega(AB)	Fraction 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*

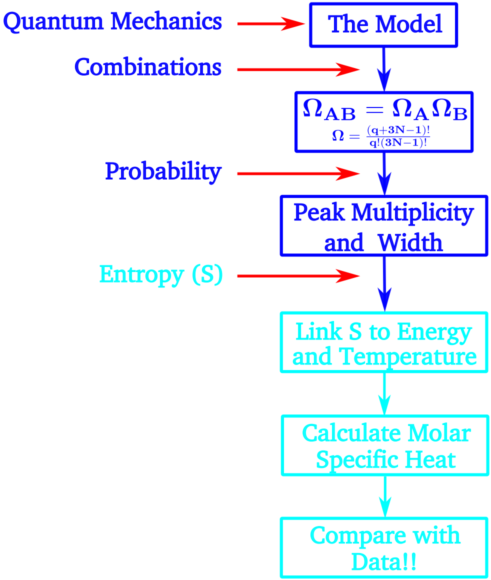
Total number of microstates: 3.096e+13

Ω_{AB} … nbined state … icities.

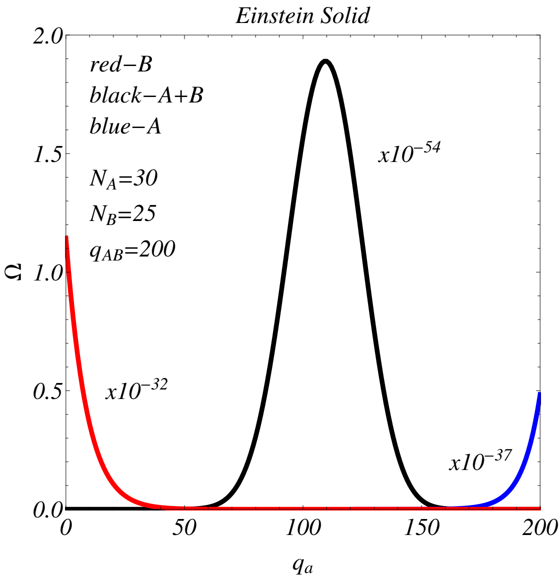
An Einstein solid is made of N, three-dimensional harmonic oscillators containing q quanta of energy.

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?

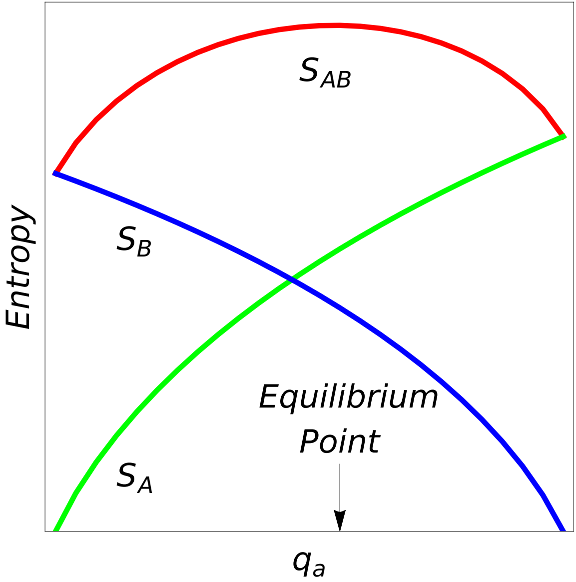
Solid	Molar Specific Heat (J/K-mole)	Our Results (J/K-mole)
Lead	26.4 ± 0.7	22 ± 6
Zinc	25.4 ± 0.6	36 ± 14
Aluminum	26.4 ± 0.2	21 ± 9
Copper	24.5 ± 0.6	25 ± 9
Tin	27.0 ± 0.6	64 ± 47
Gold	25.4 ± 0.6	
Silver	25.4 ± 0.6	
Iron	25.0 ± 0.6	


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

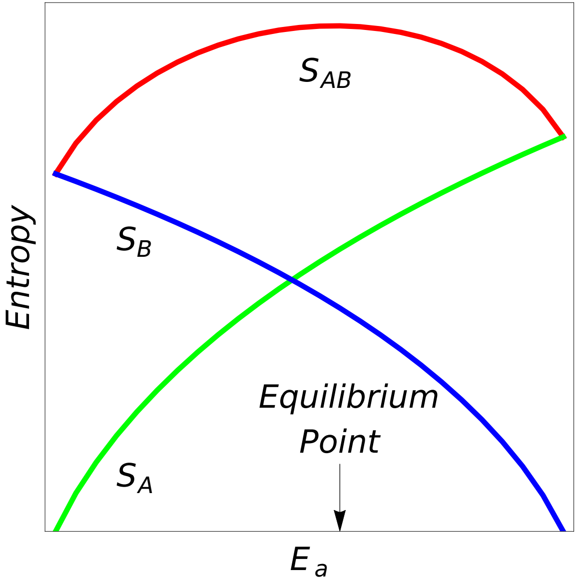


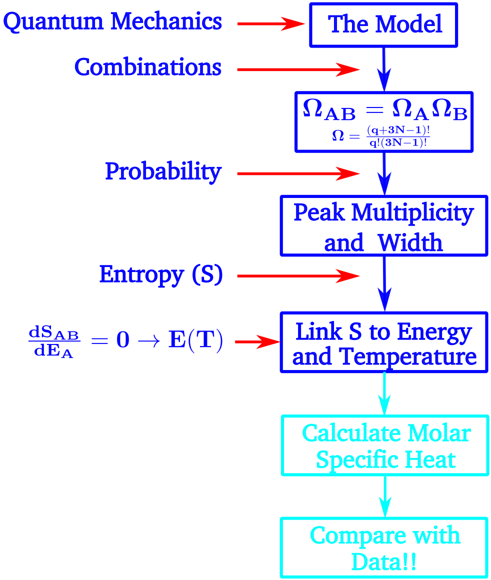
Product Rule	$\log(xy) = \log x + \log y$
Quotient Rule	$\log(\frac{x}{y}) = \log x - \log y$
Power Rule	$\log(x^p) = p \log x$
Equality Rule	If $\log x = \log y$, then $x = y$

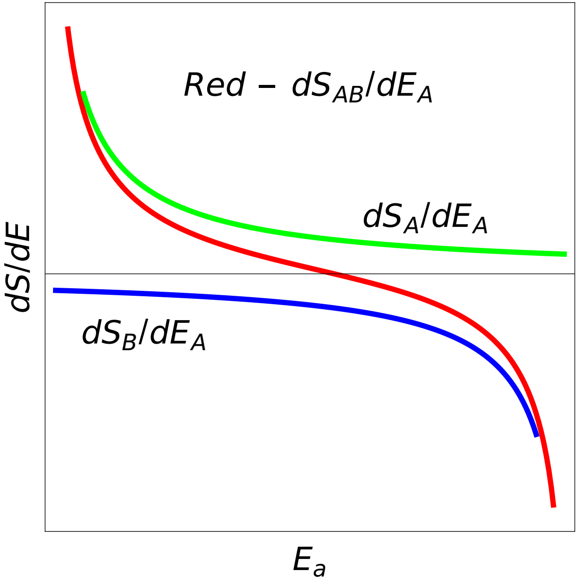


S_{AB}
S_B
S_A
Entropy
Equilibrium Point
q_a

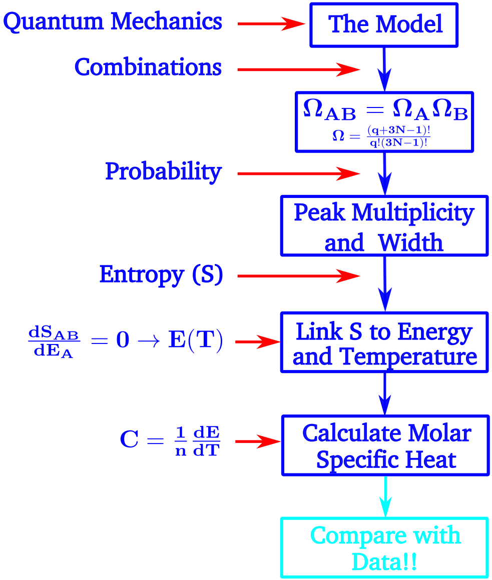
Entropy of Two Einstein Solids in Energy Terms 28




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!!


Red – dS_{AB}/dE_A
dS_A/dE_A
dS_B/dE_A
dS/dE
E_a

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!!

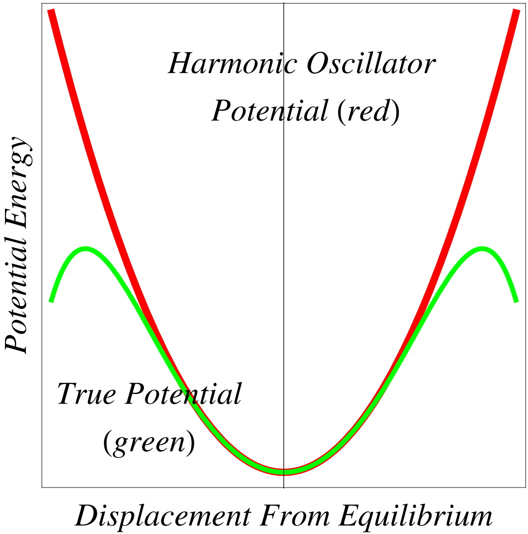
The Specific Heat of Elemental Solids

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	21 ± 9	24.9
Copper	24.5 ± 0.6	25 ± 9	24.9
Tin	27.0 ± 0.6	64 ± 47	24.9
Gold	25.4 ± 0.6		24.9
Silver	25.4 ± 0.6		24.9
Iron	25.0 ± 0.6		24.9

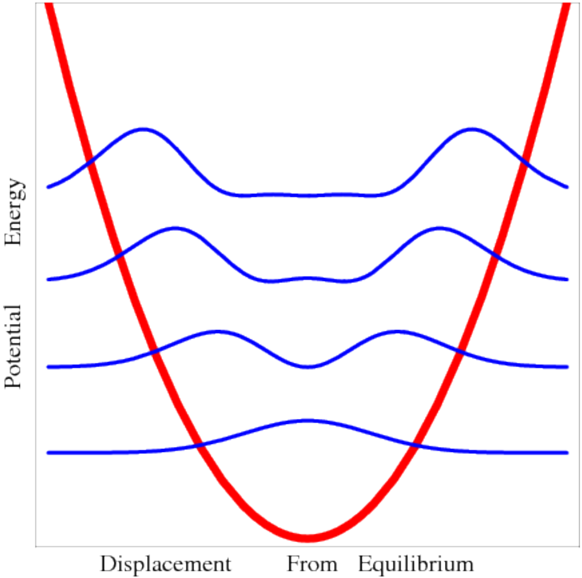
The Specific Heat of Elemental Solids 33

Imagine that the entropy of a certain substance as a function of N and E is given by the formula $S = \alpha N k_b E^3$. Using the definition of temperature, find an expression for the thermal energy E of this substance in terms of its temperature T , the number of particles N, and any other necessary constants. Use this result to calculate the molar specific heat. Are these results well behaved?

The Harmonic Oscillator Approximation 34



Quantum Oscillator



Installing Capstone

1. Go to the website

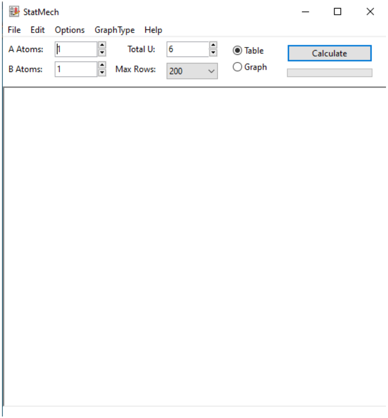
   https://www.pasco.com/downloads/capstone

   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

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.



Updating *equilib.exe* 38

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.