Announcements

- The sample final exam and associated solutions are now posted. Check "What's new?" at website!
- Sessions will be held to review homeworks and other course material and to go over the sample exam on Tuesday and Thursday at 3PM in room 428 Pupin.
- Special office hours will be held by me in my office on Friday from 10AM until 12:30PM (or later if people are waiting). I am likely also to be in my office next Monday morning (on the final date). I will also be available to answer any specific questions by e-mail.

Thermodynamics and Gases

Last Time

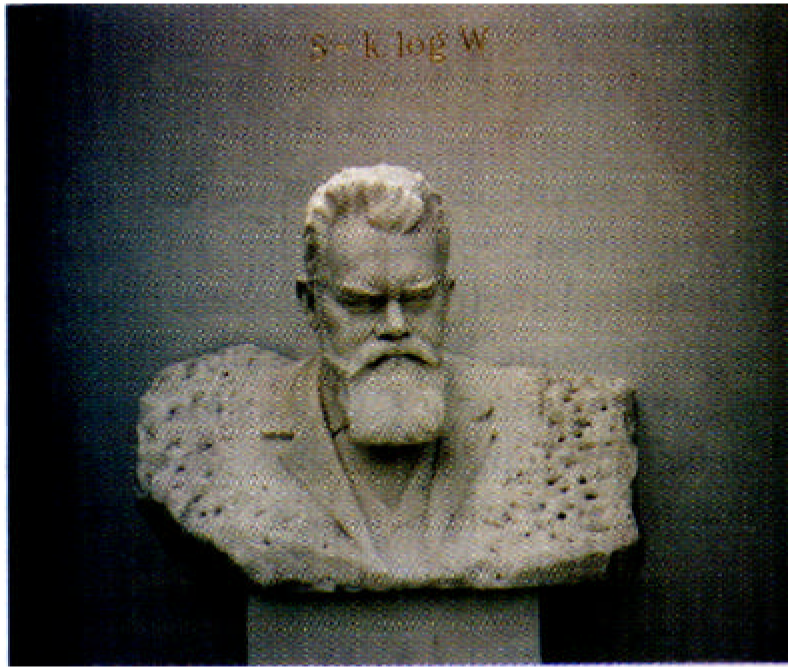
- 2nd Law of Thermodynamics
- Entropy
- Uses in engines, heat pumps, refrigerators

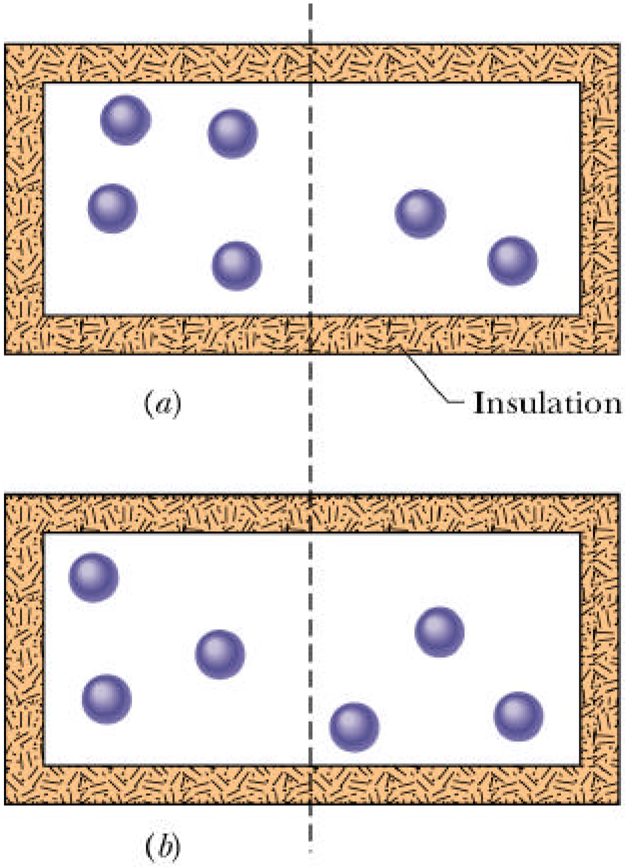
Today (not on final)

- Origin of Entropy
  - measure of system disorder
  - statistical mechanics
- Finish

review

Boltzmann: Macrostates (and Microstates)





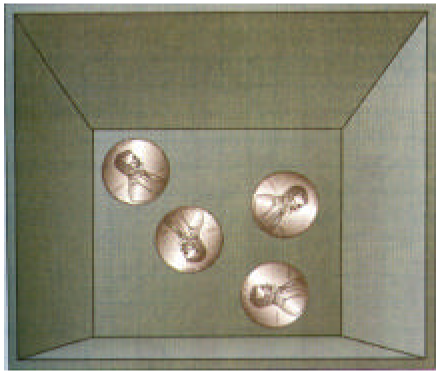
- **Two scenarios at right**
  - each has several possible microstates
  - depend on which molecules are on which side
- **Analyze with coins**

$$S = k \ln W$$

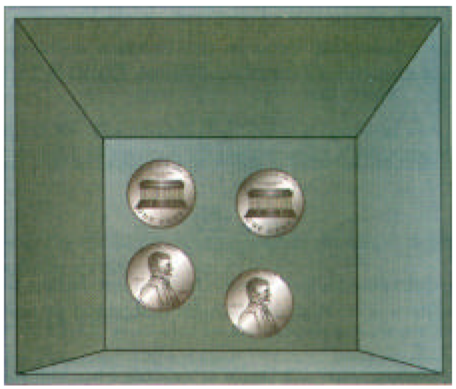
$$W = \begin{pmatrix} \text{number of} \\ \text{microstates} \end{pmatrix}$$

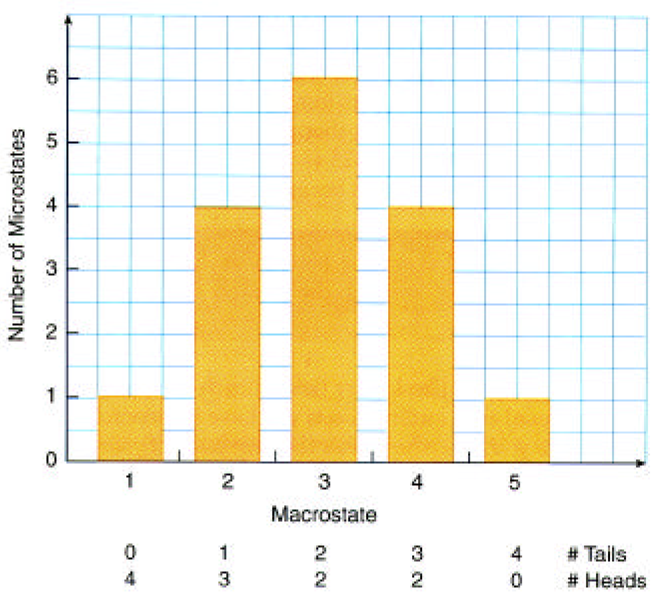
review

4 pennies-macrostates and microstates



- all heads: one microstate
- One tail: 4 microstates
- 2 heads, 2 tails: six microstates
- In total: 16 microstates
- Pix shows relative probabilities



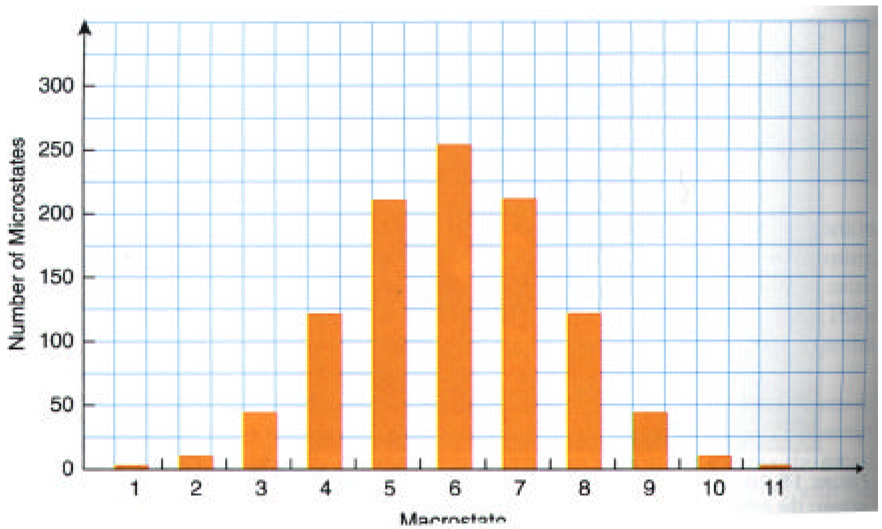


Four-Penny Macrostates and Microstates

Penny 1	Penny 2	Penny 3	Penny 4
Macrostate (1): 4 heads (H) and 0 tails (T)			
H	H	H	H
(1 microstate)			
Macrostate (2): 3 heads and 1 tail			
H	H	H	T
H	H	T	H
H	T	H	H
T	H	H	H
(4 microstates)			
Macrostate (3): 2 heads and 2 tails			
H	H	T	T
H	T	T	H
T	T	H	H
T	H	H	T
T	H	T	H
H	T	H	T
(6 microstates)			
Macrostate (4): 1 head and 3 tails			
H	T	T	T
T	H	T	T
T	T	H	T
T	T	T	H
(4 microstates)			
Macrostate (5): 0 heads and 4 tails			
T	T	T	T
(1 microstate)			

review

10 coins - contrast



crostate	H	T	# microstates Ω
1	10	0	1
2	9	1	10
3	8	2	45
4	7	3	120
5	6	4	210
6	5	5	252
7	4	6	210
8	3	7	120
9	2	8	45
10	1	9	10
11	0	10	1
		Total	$1024 = 2^{10}$

- 5 each is 252 times more probable than all heads
- as more coins are added, equal partitioning=equal numbers heads and tails gets more probable relative to all other possibilities
  - especially those near the extremes (list top and bottom)

Increasing the coins

TABLE 15-2
Probabilities of Various Macrostates for 100 Coin Tosses

Macrostate		Number of Microstates, W
Heads	Tails	
100	0	1
99	1	1.0×10^{2}
90	10	1.7×10^{13}
80	20	5.4×10^{20}
60	40	1.4×10^{28}
55	45	6.1×10^{28}
50	50	1.0×10^{29}
45	55	6.1×10^{28}
40	60	1.4×10^{28}
20	80	5.4×10^{20}
10	90	1.7×10^{13}
1	99	1.0×10^{2}
0	100	1

- **As the number of coins increases, equal numbers as heads/tails is more and more probable relative to others**

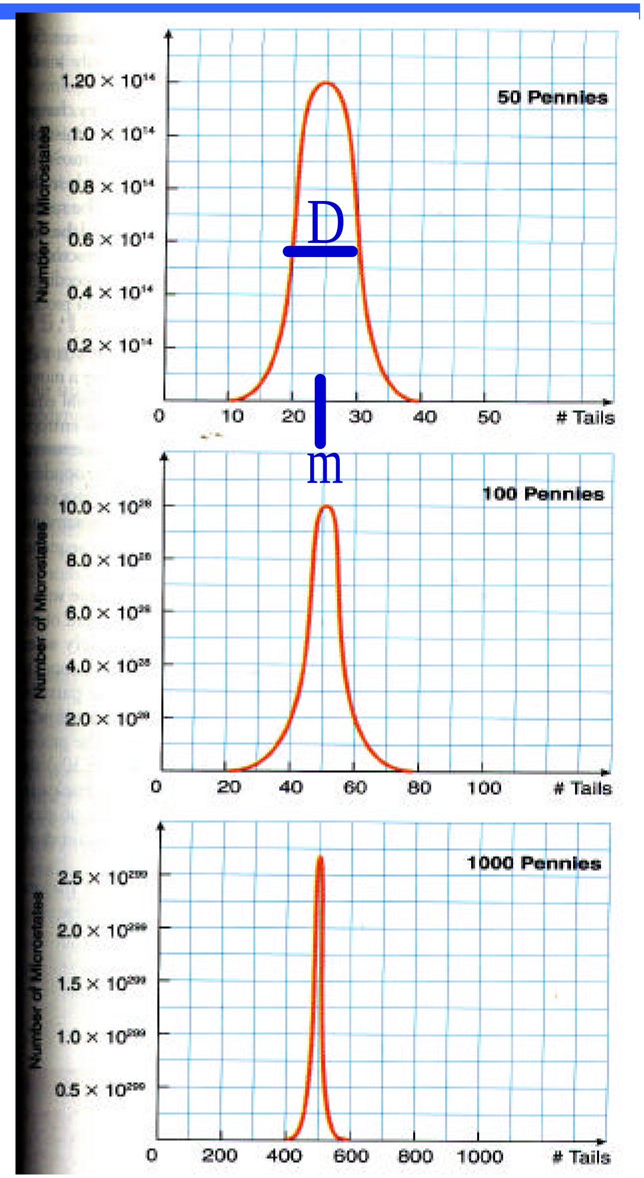
Note: binomial dist.

$$W = \frac{N!}{n_1!\, n_2!}$$

Ratio width to mean of parameter

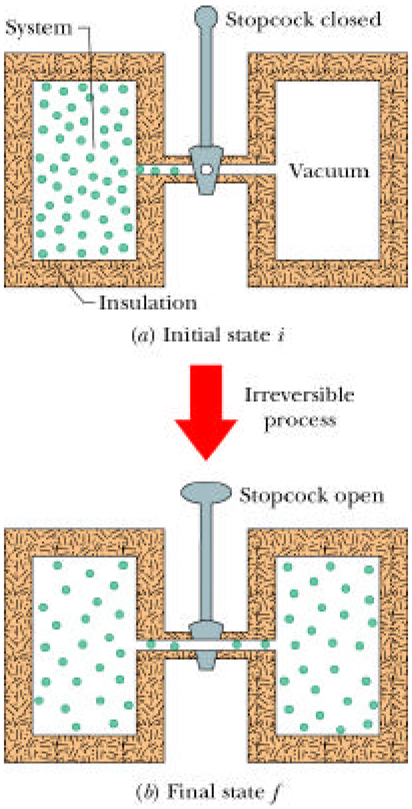
$$\frac{\Delta}{m} \propto \frac{1}{\sqrt{N}}$$

With atoms we deal with ~ 10^{24} atoms

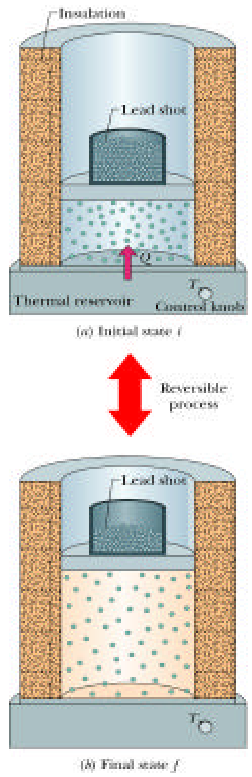


review

Entropy increase of free expansion of gas from Thermodynamics



irreversible in a closed system



reversible isothermal equivalent

$$\Delta S = \frac{Q}{T} = \frac{W}{T} = \frac{nRT}{T}\ln\frac{V_f}{V_i}$$

$$\Delta S = nR\ln\frac{V_f}{V_i}$$

- This is the entropy change of the gas for <u>both processes</u>
- more general

entropy change for ideal gas

$$\Delta S = \int_i^f \frac{dQ}{T} = nC_V\int_{T_i}^{T_f}\frac{dT}{T} + nR\int_{V_i}^{V_f}\frac{dV}{V}$$

$$\Delta S = nC_V\ln\frac{T_f}{T_i} + nR\ln\frac{V_f}{V_i}$$

Boltzmann applied = Statistical Mechanics

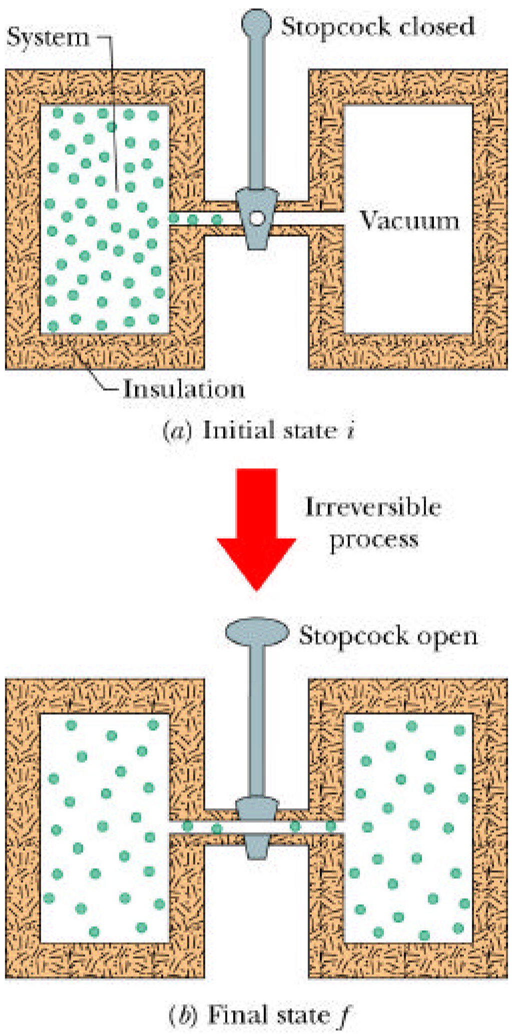
- More microstates = more entropy
- For atoms and microstates, the number of states are delineated by
  - Position possibilities
  - Velocity possibilities
- for each atom, enormous number of possibilities
- Total entropy = Sum over all atoms (also enormous number)
- Have looked at simpler physical system: limited number of coins – states of up or down

$$S_{molecule} = k \ln w$$

w = # microscopic states in macrostate

$$S_{gas} = \sum_{\substack{all \\ molecules}} S_{molecule} \qquad \Delta S_{1\to 2} = Nk\left[\ln w_2 - \ln w_1\right] = Nk \ln\left(\frac{w_2}{w_1}\right)$$

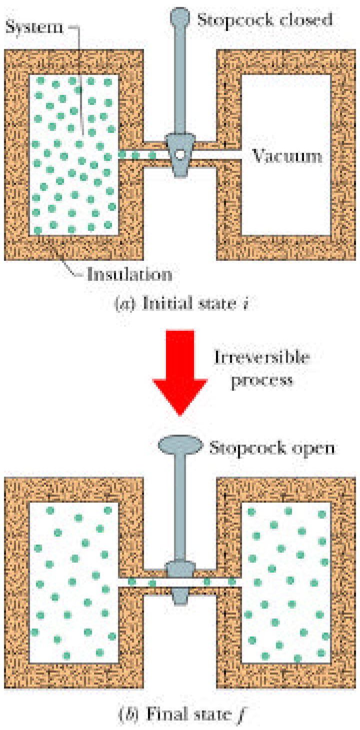
Position states available depends on Volume



- **Pix shows gas expanding to new volume: getting many more position states available**
- **In general, same atom in volume V_f has many more position states available than at volume V_i . ($w \mu V$)**
- **Ratio of number of available position states is V_f / V_i .**

$$\frac{\text{No states } V_f}{\text{No states } V_i} = \left(\frac{V_f}{V_i}\right)$$

Entropy of Isothermal Expansion from Stat Mech



- Ratio of number of position states is V_f / V_i .

$$\frac{\text{No states } V_f}{\text{No states } V_i} = \left(\frac{V_f}{V_i}\right)$$

$$\Delta S_{j^{th}\ \text{molecule}} = k \ln\left(\frac{V_f}{V_i}\right)$$

$$\Delta S = \sum_{j=1}^{N} \Delta S_j = Nk \ln\left(\frac{V_f}{V_i}\right)$$

$$\Delta S = nR \ln\left(\frac{V_f}{V_i}\right)$$

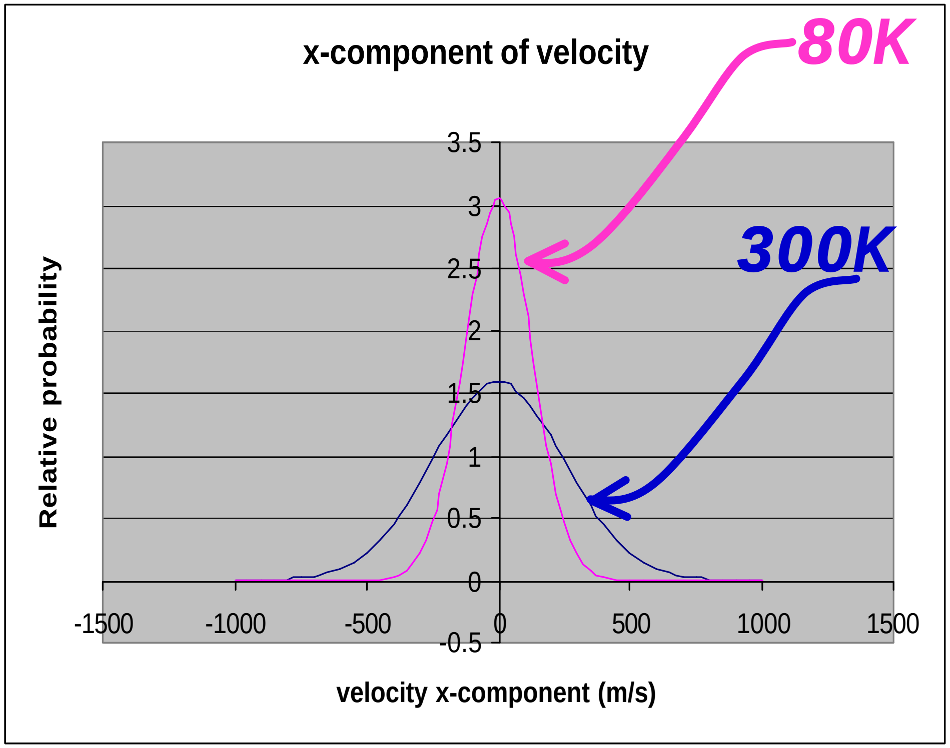
entropy change for isothermal gas expansion from using thermodynamics

$$\Delta S = nR \ln\frac{V_f}{V_i}$$

Temp Changes: Velocity States Available depends on Temperature

$$dP(v_x) = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{mv_x^2}{2kT}} dv_x$$ Gaussian

$$\langle v_x \rangle = 0 \qquad \sigma_{v_x} = \sqrt{\frac{kT}{m}}$$



- Number of v_x states available to noble gas atom is proportional to σ_{vx}
- Number of available velocity states proportional to $\sigma_{vx} * \sigma_{vy} * \sigma_{vz}$

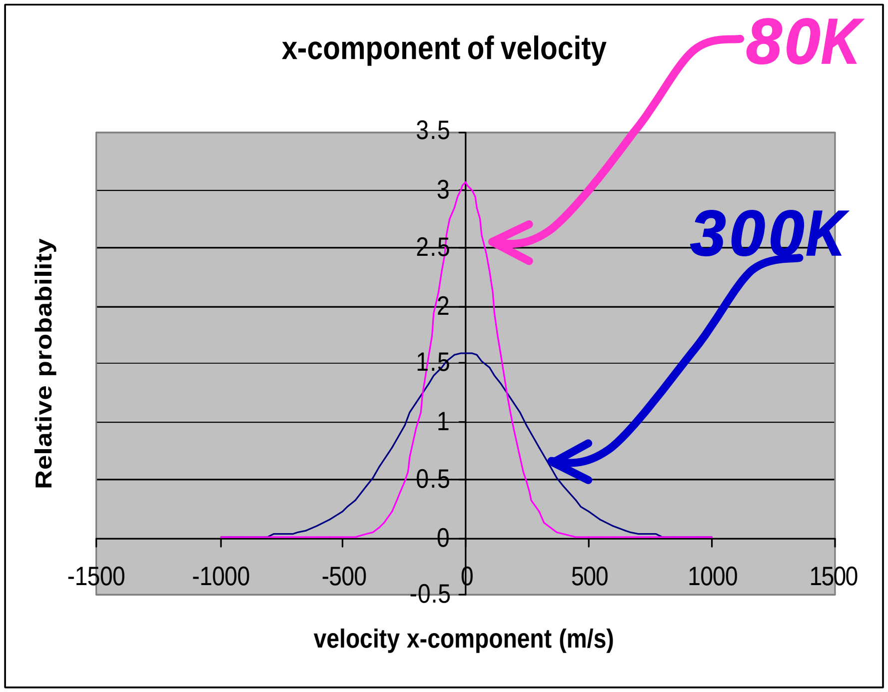
$$\sigma_{v_x} = \sqrt{\frac{kT}{m}}$$

$$\sigma_{v_x}\sigma_{v_y}\sigma_{v_z} = \left[\frac{kT}{m}\right]^{\frac{3}{2}}$$

$$\frac{\text{No states } T_f}{\text{No states } T_i} = \left(\frac{T_f}{T_i}\right)^{\frac{3}{2}}$$

Entropy Change for Temperature Change of monatomic gas from Stat Mech

$$dP(v_x) = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{mv_x^2}{2kT}} dv_x$$ Gaussian



entropy change for isochoric change from using thermodynamics

$$\Delta S = nC_V \ln \frac{T_f}{T_i}$$

- Number of available velocity states proportional to $S_{vx} * S_{vy} * S_{vz}$

$$S_{v_x} S_{v_y} S_{v_z} = \left[\frac{kT}{m}\right]^{\frac{3}{2}}$$

$$\frac{\text{No states } T_f}{\text{No states } T_i} = \left(\frac{T_f}{T_i}\right)^{\frac{3}{2}}$$

$$\Delta S_{1 \text{ molecule}} = k \ln \left(\frac{T_f}{T_i}\right)^{\frac{3}{2}}$$

$$\Delta S = Nk \ln \left(\frac{T_f}{T_i}\right)^{\frac{3}{2}}$$

$$\Delta S = \frac{3}{2} Nk \ln \left(\frac{T_f}{T_i}\right) = nC_V \ln \left(\frac{T_f}{T_i}\right)$$

Check Stat Mech vs Thermo

Stat mech - Vol. chg

$$\frac{\text{No states } V_f}{\text{No states } V_i} = \left(\frac{V_f}{V_i}\right)$$

$$\Delta S_{1\ \text{molecule}} = k \ln\left(\frac{V_f}{V_i}\right)$$

$$\Delta S = Nk \ln\left(\frac{V_f}{V_i}\right)$$

$$\Delta S = nR \ln\left(\frac{V_f}{V_i}\right)$$

thermodynamics

entropy change for ideal gas

$$\Delta S = \int_i^f \frac{dQ}{T} = nC_V \int_{T_i}^{T_f} \frac{dT}{T} + nR \int_{V_i}^{V_f} \frac{dV}{V}$$

$$\Delta S = nC_V \ln\frac{T_f}{T_i} + nR \ln\frac{V_f}{V_i}$$

Stat mech = temp chg

$$\sigma_{v_x}\sigma_{v_y}\sigma_{v_z} = \left[\frac{kT}{m}\right]^{\frac{3}{2}}$$

$$\frac{\text{No states } T_f}{\text{No states } T_i} = \left(\frac{T_f}{T_i}\right)^{\frac{3}{2}}$$

$$\Delta S_{1\ \text{molecule}} = k \ln\left(\frac{T_f}{T_i}\right)^{\frac{3}{2}}$$

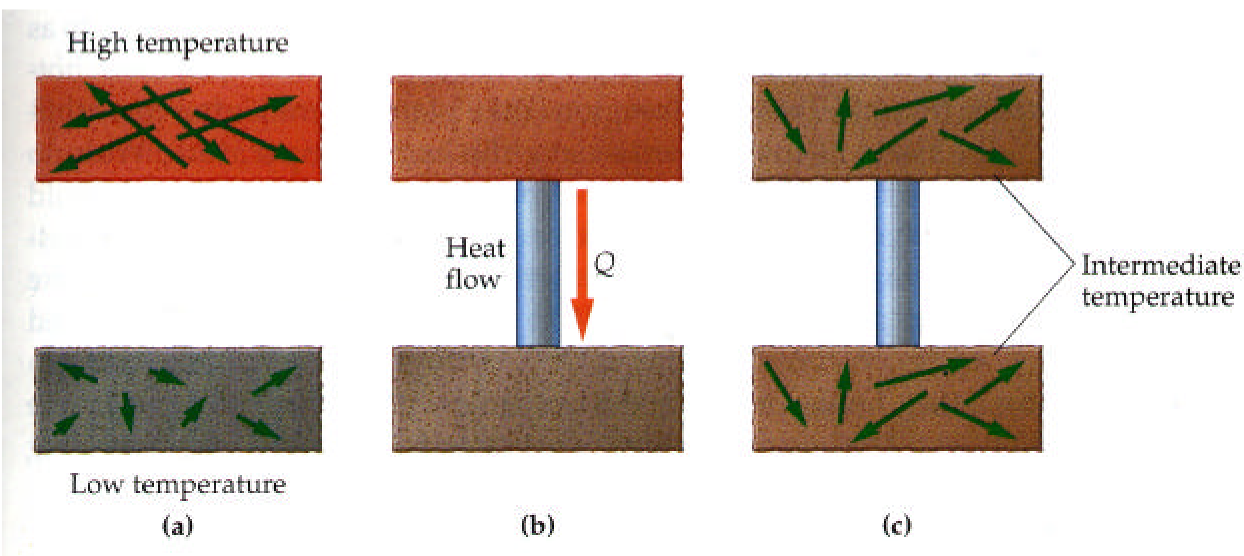
$$\Delta S = Nk \ln\left(\frac{T_f}{T_i}\right)^{\frac{3}{2}}$$

$$\Delta S = \frac{3}{2} Nk \ln\left(\frac{T_f}{T_i}\right)$$

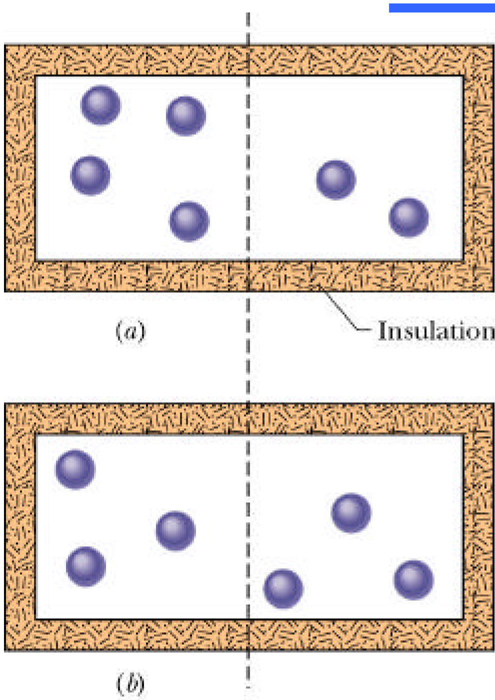
$$\Delta S = nC_V \ln\left(\frac{T_f}{T_i}\right)$$

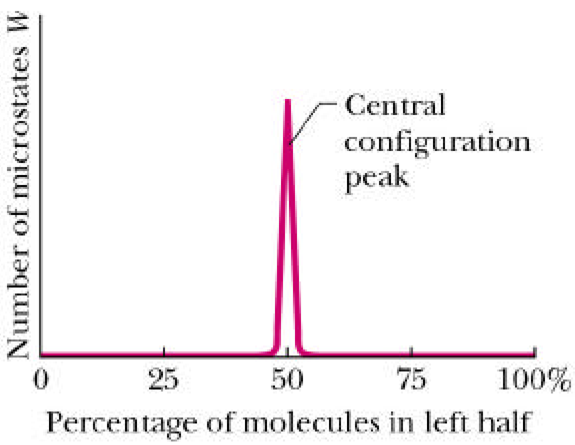
Statistical Requirement

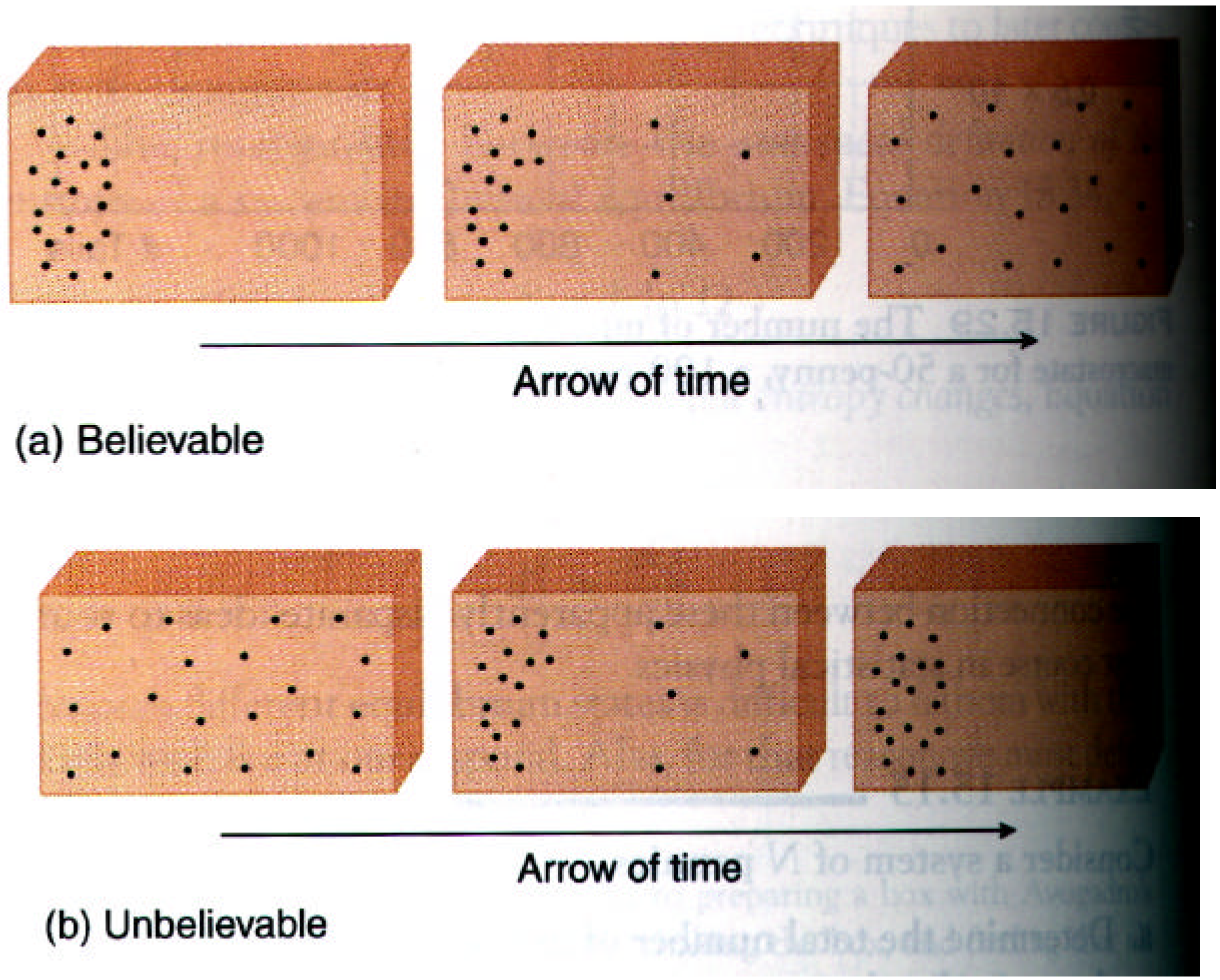
- Systems will evolve from <u>less probable macrostate</u> to <u>most probable macrostate</u>
- Entropy will always increase
- Ordered segregation will inexorably become disordered equilibrium



Molecules in a box







Exceptions?

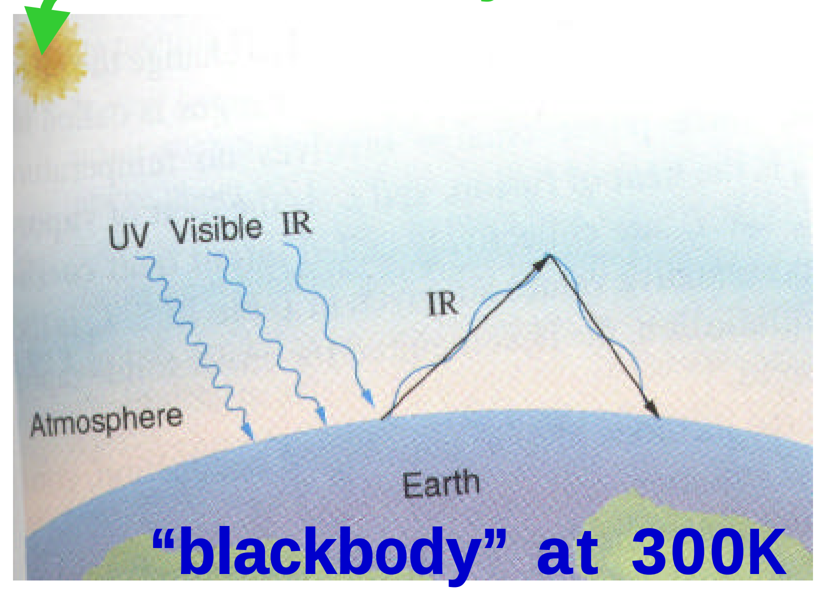
- Do living organisms <u>violate</u> entropic principles?
- Does evolution of life <u>violate</u> entropic principles?

NO!

Entropy of the world increases in <u>every</u> process!

Evolution of life does not contradict physical principles!

"blackbody" at 5800K



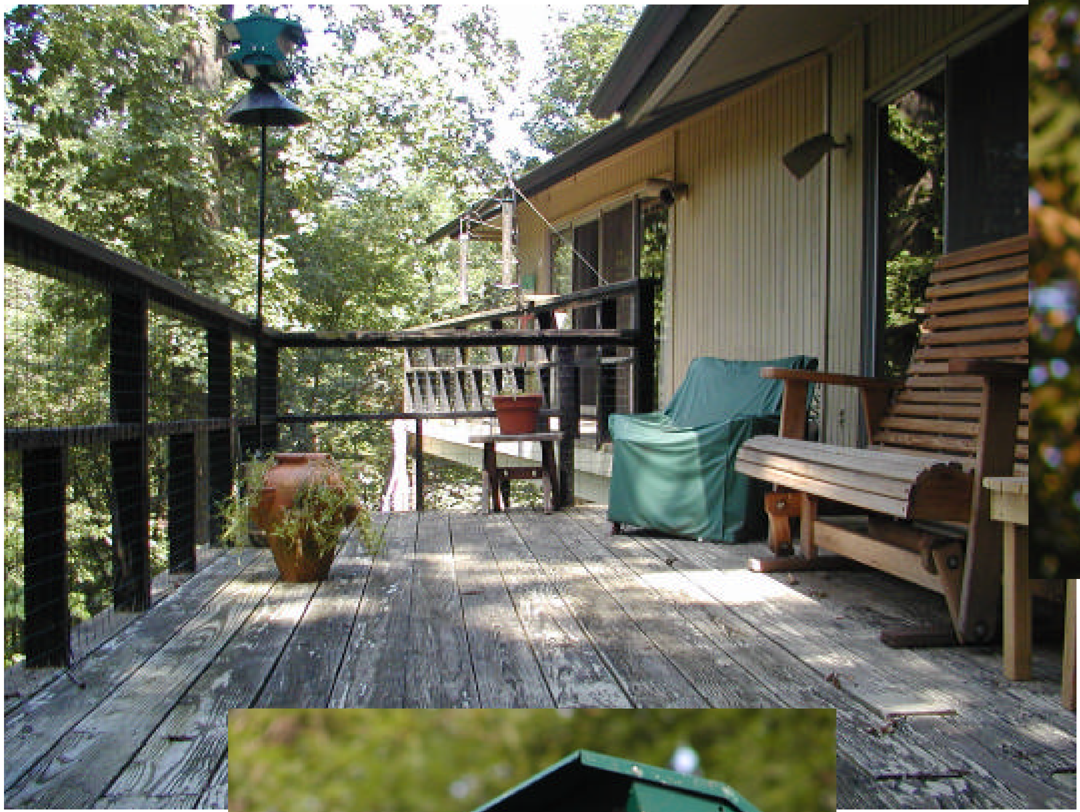
"blackbody" at 300K

That’s Almost All

- Last lecture
- Different lecturer next semester
- Before leave … one more story of personal nature (with a moral)

1 - wildlife

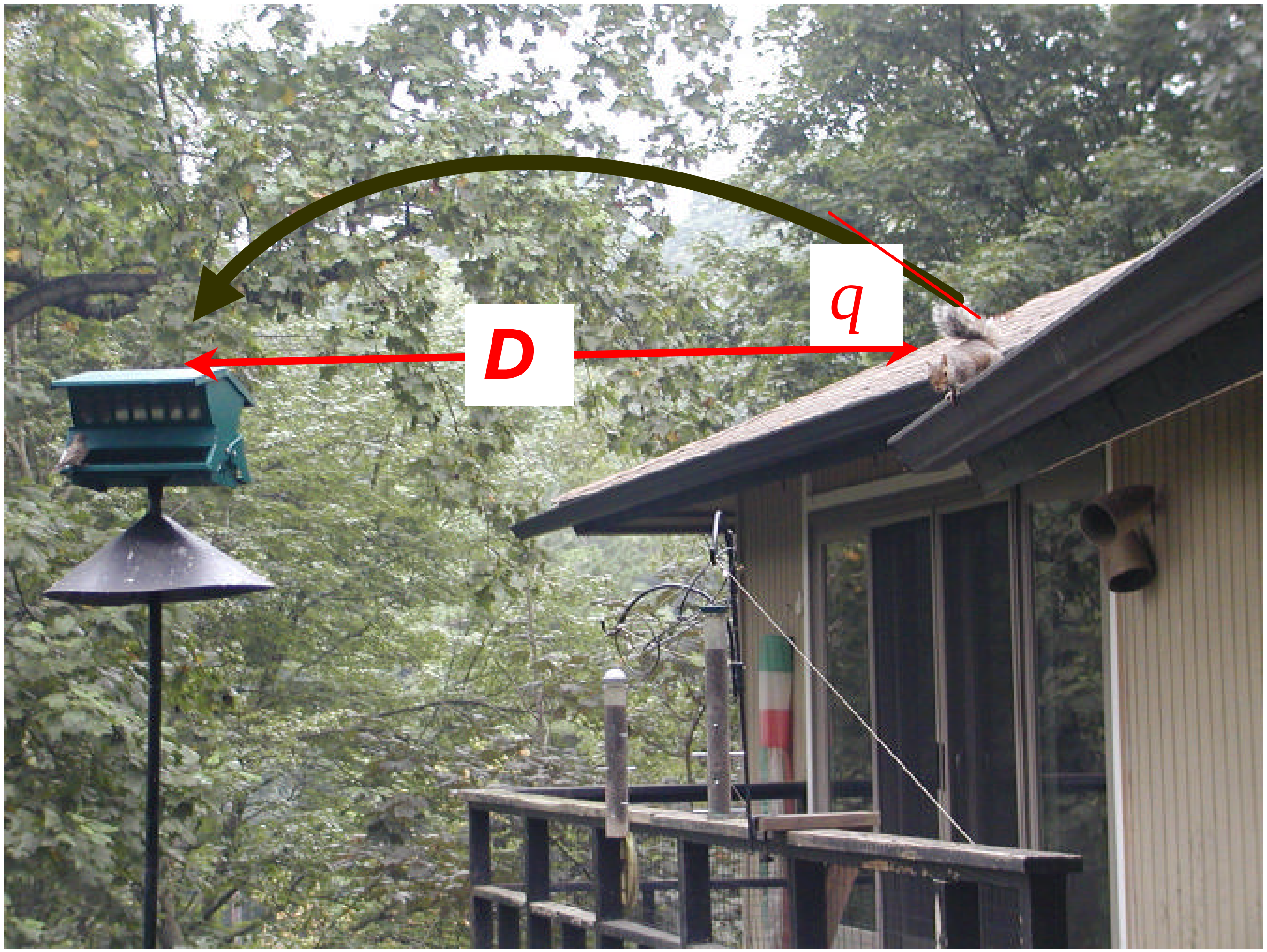
2 - bird feeder & birds



3 – who's in charge?

4 – not me, that's for sure!

5 – how does squirrel make it?



Implications for the jump:

In simple model, the coefficient of kinetic friction at the feeder must be large enough to stop the horizontal momentum of the squirrel

$$m_k > \frac{1}{\tan q}$$

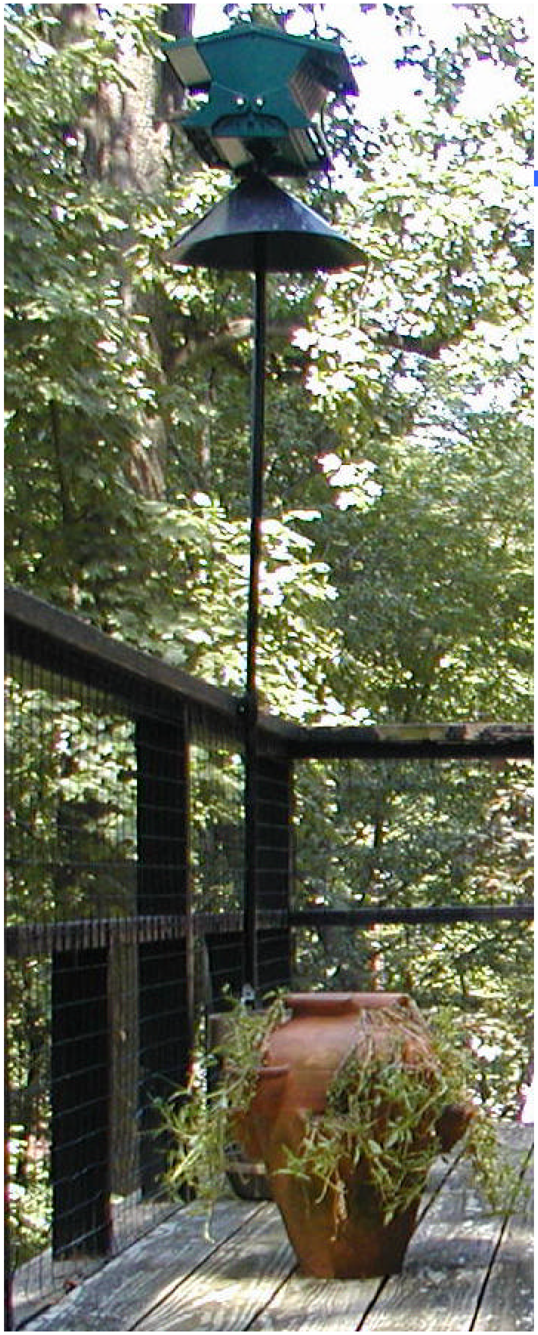
Solution: make top of feeder slippery

6 – They still get there!

7 – An experimental result

Moral of the Story

- Learn all the established principles
- Know where they come from and how to apply them
- **But check them out**
  - With experiments
  - With observations



Surrender… Solution: no seed in the feeder!

- no food
- no squirrels
- no birds

- unhappy birds
- unhappy squirrels

9: Revenge

- tap, tap,tap
- on my chamber door
- outside my window

That's All

- Have a good final!
- Have a good second semester!
- Best of fortune in the future!
- Please remain to fill in Questionaire