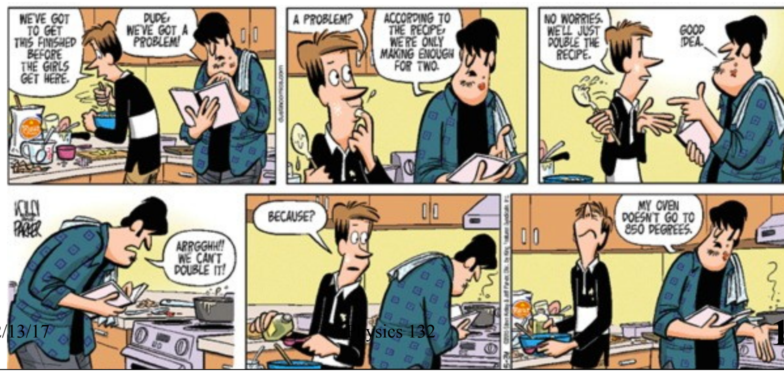
February 13, 2017 Physics 132 Prof. E. F. Redish

- **Theme Music:** **Jake Shimabukuro**
  Shake it up
- **Cartoon:** **Steve Kelley & Jeff Parker**
  Justin



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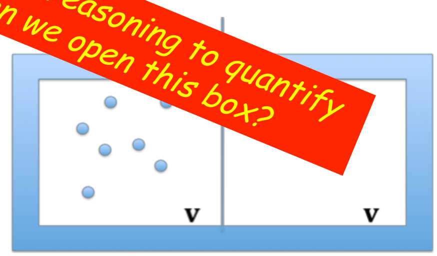
Suppose an isolated box of volume $2V$ is divided into two equal compartments. An ideal gas occupies half of the container and the other half is empty. When the partition separating the two halves of the box is rem[illegible] and the system reaches equilibrium again, how [illegible] **entropy** of the gas compare to the entropy o[illegible]tem?

1. The entropy increases
2. The entropy decreases
3. The entropy stays the same
4. There is not enough information to determine the answer



Can we use the same kind of reasoning to quantify the change in entropy when we open this box?

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Foothold ideas: Exponents and logarithms

- Power law: $f(x) = x^2 \quad g(x) = Ax^7$
  a variable raised to a fixed power.
- Exponential: $f(x) = e^x \quad g(N) = 2^N \quad h(z) = 10^z$
  a fixed constant raised to a variable power.
- Logarithm: the inverse of the exponential.

$$x = e^{\ln(x)} \qquad x = \ln\left(e^x\right)$$

$$y = 10^{\log(y)} \qquad y = \log\left(10^y\right)$$

$\log(2) = 0.3010$

$\log(e) = 0.4343$

$2^N = \left(10^{0.3010}\right)^N \approx 10^{0.3N}$

$e^x = \left(10^{0.4343}\right)^x \approx 10^{0.4x}$

$2^N = B$

$N \log 2 = \log B \Rightarrow N = \dfrac{\log B}{\log 2}$

Logs convert multiplying to adding!

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Doubling the size of the box

- Consider each side of the box as being broken into M small volumes. We can put a molecule into one of these volumes in M different ways.
- So to put N particles into the box we can put them in in MxMxM...xM (N times) different ways. $W_1 = M^N$.
- If we have 2 boxes we can put them each into the bigger box in 2^M different ways.
- So to put N particles into the double box, $W_2 = (2M)^N = 2^N M^N = 2^N W_1$
- What does this say about the change in entropy when the size of the box is doubled?

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Doing the calculation: Doubling the size of the box

- $W_1 = M^N$
- $W_2 = (2M)^N = 2^N M^N = 2^N W_1$
- What does this say about the change in entropy when the size of the box is doubled?
- $S_1 = k_B \ln W_1$
- $S_2 = k_B \ln W_2 = k_B (N \ln 2 + \ln W_1) = k_B N \ln 2 + S_1$

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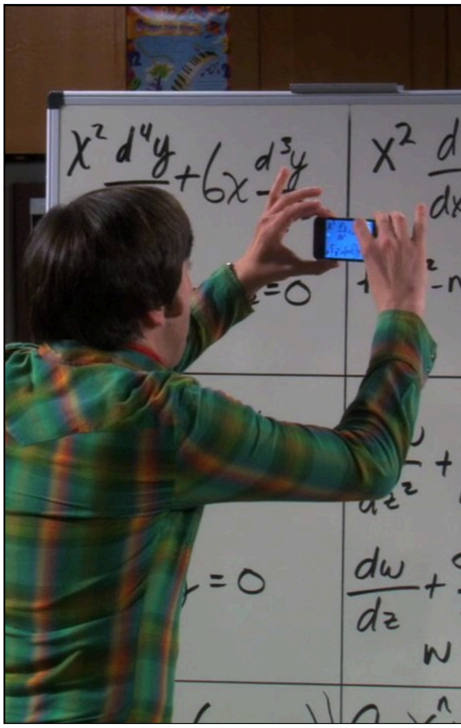

The Equation of the Day

Gibbs Free Energy

$$\Delta G = \Delta H - T\Delta S$$

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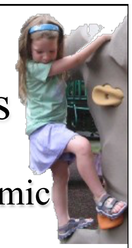
Foothold ideas:
The Second Law of Thermodynamics



- Systems spontaneously move toward the thermodynamic (macro)state that correspond to the largest possible number of particle arrangements (microstates).
  - The 2^{nd} law is probabilistic. Systems show fluctuations – violations that get proportionately smaller as N gets large.
- Systems that are not in thermodynamic equilibrium will spontaneously transform so as to increase the entropy.
  - The entropy of any particular system can decrease as long as the entropy of the rest of the universe increases more.
- The universe tends towards states of increasing chaos and uniformity. (Is this contradictory?)

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Conclusion

- If energy packets are randomly fluctuating through all DoFs with equal probability, then each microstate will be equally probable.
- Some macrostates (distributions of energy between blocks of the system) are more likely.
- Thermal energy is more likely to flow from a hot object to a cold object than vice versa – and the more DoFs there are, the stronger this tendency will be.

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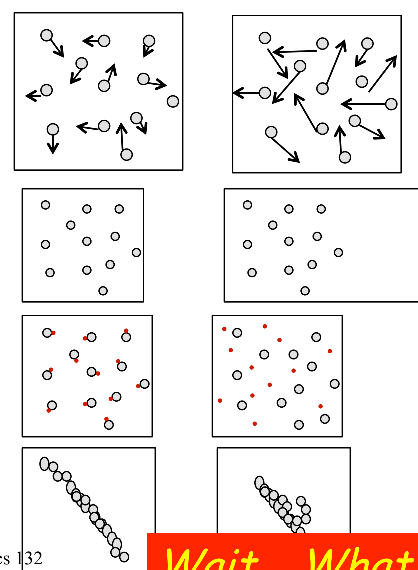
Ways to increase entropy

- Add energy
- Add volume
- Dissociate molecules
- Curl up a linear molecule



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Wait... What?!

Conditions on a spontaneous change due to energy exchange

- Consider some system spontaneously transforming by exchanging some energy, $\Delta U_{sys} = Q$, with its environment.
  Two conditions must be met:
- First law: $\Delta U_{sys} + \Delta U_{env} = 0$
- Second law: $\Delta S_{sys} + \Delta S_{env} \geq 0$
- Entropy-energy relation: $\Delta S_{env} = \dfrac{\Delta U_{env}}{T} = -\dfrac{\Delta U_{sys}}{T}$

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These let us express the condition on the change of entropy of the universe in terms of the system alone.

$$\Delta S_{env} = -\frac{\Delta U_{sys}}{T}$$

$$\Delta S_{sys} + \Delta S_{env} = \Delta S_{sys} - \frac{\Delta U_{sys}}{T} \geq 0$$

$$T\Delta S_{sys} - \Delta U_{sys} \geq 0$$

$$\Delta F \equiv \Delta U_{sys} - T\Delta S_{sys} \leq 0$$

If we are operating at constant pressure, we want to use enthalpy, ΔH, instead of internal energy, ΔU. This yields Gibbs FE (G) instead of Helmholtz FE (F).

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Foothold ideas: Transforming energy

- Internal energy: thermal plus chemical ΔU
- Enthalpy: internal plus amount needed to make space at constant *p* $\Delta H = \Delta U + p\Delta V$
- Gibbs free energy: enthalpy minus amount associated with raising entropy of the rest of the universe due to energy dumped $\Delta G = \Delta H - T\Delta S$
- A (constant pressure) process will go spontaneously if $\Delta G < 0$ (rolling down the free energy hill).

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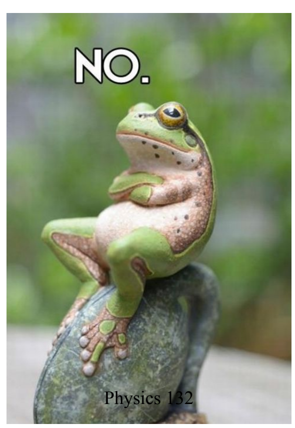
Reading question

- Is Gibbs free energy conserved like all other energy?



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