Notes for today

- Reminder, web address: rossgroup.tamu.edu/408page.html
  Has HW, syllabus, slides posted.
- Reading: starting ch. 15. Today we will discuss the probabilities going into problems 4 and 5.
- I am still looking for a volunteer for problems 5 and 6.
- Lecture recordings etc.: Reminder again that you should let me know if you have a Covid quarantine (or other University excuse). I can share lecture recording or a zoom link to view the lecture in real time. I am still experimenting with various improvements for the zoom recording.

Recall: Ideal gas

$U = \frac{3}{2} N k_B T.$ Energy (ideal gas specific case)

$PV = N k_B T.$ Equation of state (ideal gas specific case.

vs General Relationships (for all systems, but recall these are for controlled processes):

$$dU = TdS - PdV + \mu dN$$

$$dS = \frac{1}{T} dU + \frac{P}{T} dV - \frac{\mu}{T} dN$$

$S = S(U, V, N)$ or $U = U(S, V, N)$ [fundamental equation]

With $T = \left(\frac{\partial U}{\partial S}\right)_{VN}$ $etc. \Rightarrow$ complete model of behavior.

Entropy define: $S \equiv k_B ln(\Omega)$ (Boltzmann)

- Fundamental assumption of statistical mechanics
- As before we assume equilibrium; then Ω = **multiplicity**, defined as *number of accessible states* (e.g. # of states at a given total energy, spatially accessible by particles in container volume, without violating known N, etc.)
- Classically states counted by "phase space bins" $d^3r \cdot d^3p$; in QM Ω counts number of eigenstates. Terminology – *microstate:* locally defined state (all quantum numbers) *macrostate:* specified by macroscopic parameters.
- Note, QM superposition is not the same thing, this is a "mixed state".

  $\psi_1 + \psi_2$ vs. $\psi_1 + e^{i\phi}\psi_2$: phase is random/rapidly changing: incoherent sum
- Extensive property: can see from definition.

Entropy define: $S \equiv k_B ln(\Omega)$ (Boltzmann)

- Fundamental assumption of statistical mechanics
- As before we assume equilibrium; then Ω = **multiplicity**, defined as *number of accessible states* (e.g. # of states at a given total energy, spatially accessible by particles in container volume, without violating known N, etc.)

Fundamental Postulate of Statistical Mechanics:

Over time an isolated system in equilibrium will be found in **each accessible microstate** with **equal probability**.

Ergodic hypothesis invoked here: all states that can be visited *will* be visited. Difficult to justify in detail; possibly not needed when very large numbers of states are involved.

Second Law of Thermodynamics:

Spontaneous processes always tend toward a macrostate with the largest number of accessible microstates; e.g. spontaneous processes have $\Delta S \geq 0$ (total entropy for all interacting systems, increases overall entropy of everything — isolated system, or "entropy of universe")

- Separate law of nature based on observed behavior, not derived from physics of microscopic behavior.

- Examples include free expansion; over-writing great novel on your laptop by random bits; mixing sugar and salt.

Probabilities and multiple events:

probability of *n* events occurring in *N* turns:

$$P = (p_{event})^n (p_{no-event})^{N-n} \frac{N!}{n!(N-n)!}$$

- # permutations = multiplicity Ω, for a single type of process (or for identical particles occupying multiple states) [ideal gas in phase space “bins”, “phonon” vibrational excitations,…]
- More generally, need *product* of multiplicities (e.g. 2 systems taken together, 2 distinguishable types of particles, etc.)
- Note 2-state system of ch. 15 is distinguishable.

Example: for sequence of coin flips, what is probability of H-T-T-T in order?
Probability of 2H & 2T, any order?

Large numbers:

probability of *n* events occurring in *N* turns:

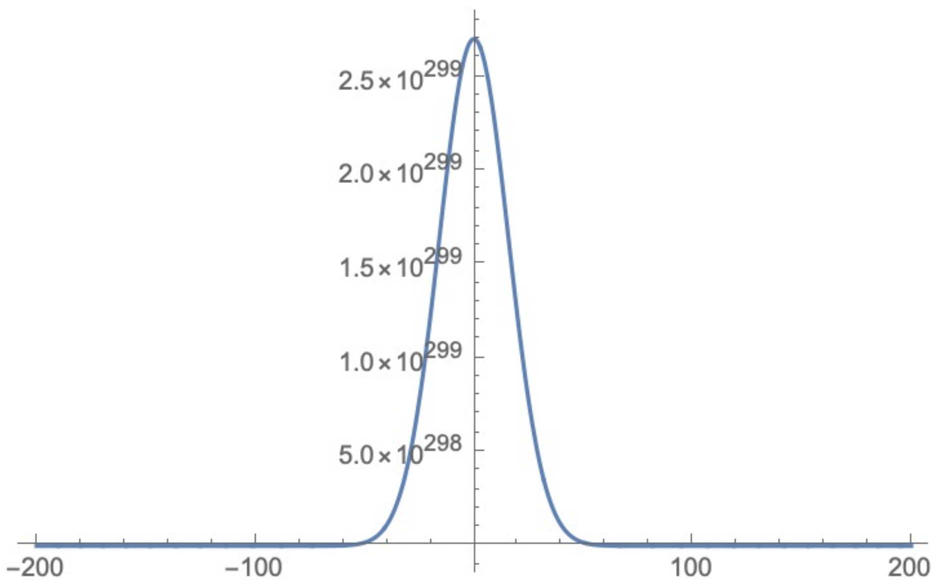
$$P = (p_{event})^n (p_{no-event})^{N-n} \frac{N!}{n!(N-n)!}$$

For large N equivalent to Gaussian distribution; relative width shrinks $\propto 1/\sqrt{N}$

```
N[1000! / (500! × 500!)]
```

2.70288×10^{299}

```
Plot[1000! / ((500 + n)! (500 - n)!), {n, -200, 200}, PlotRange -> All]
```



See e.g. Reif text.

Binomial distribution, large N:

Recall $P_{n_1} = \binom{N}{n_1} p^{n_1}(1-p)^{N-n_1}$ normalized probability, n_1 successes.

Binomial theorem, $(p+q)^N = \sum_{n_1=0}^{N} \binom{N}{n_1} p^{n_1} q^{N-n_1}$

- So: $\langle n_1 \rangle = p \frac{\partial}{\partial p} \sum_{n_1=0}^{N} \binom{N}{n_1} p^{n_1} q^{N-n_1} = Np$ easy to show.

Binomial distribution, large N:

Recall $P_{n_1} = \binom{N}{n_1} p^{n_1}(1-p)^{N-n_1}$ normalized probability, n_1 successes.

Binomial theorem, $(p+q)^N = \sum_{n_1=0}^{N} \binom{N}{n_1} p^{n_1} q^{N-n_1}$

- So: $\langle n_1 \rangle = p \frac{\partial}{\partial p} \sum_{n_1=0}^{N} \binom{N}{n_1} p^{n_1} q^{N-n_1} = Np$ easy to show.

- width of peak: $\langle {n_1}^2 \rangle = p \frac{\partial}{\partial p} p \frac{\partial}{\partial p} \sum_{n_1=0}^{N} \binom{N}{n_1} p^{n_1} q^{N-n_1}$

$$= p \frac{\partial}{\partial p} [Np(p+q)^{N-1}]$$

$$\rightarrow Np[Np+q] = \langle n_1 \rangle^2 + Npq$$

Further note on Binomial distribution, large N:

Multiplicity: sufficient for fixed-energy systems (microcanonical ensemble this chapter).

Recall $P_{n_1} = \binom{N}{n_1} p^{n_1}(1-p)^{N-n_1}$ normalized probability, n_1 successes.

Probabilities important for distribution of possible energies (Canonical ensemble & Boltzmann distribution, ch. 16)

Binomial theorem, $(p+q)^N = \sum_{n_1}^{N}$

- So: $\langle n_1 \rangle = p\frac{\partial}{\partial p}\sum_{n_1=0}^{N}\binom{N}{n_1}p^{n_1}q^{N-n_1} = \mathrm{Np}$ easy to show.

- width of peak: $\langle {n_1}^2 \rangle = p\frac{\partial}{\partial p}p\frac{\partial}{\partial p}\sum_{n_1=0}^{N}\binom{N}{n_1}p^{n_1}q^{N-n_1}$

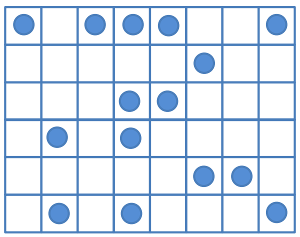
$$= p\frac{\partial}{\partial p}[Np(p+q)^{N-1}]$$

$$\to Np[Np+q] = \langle n_1 \rangle^2 + Npq$$

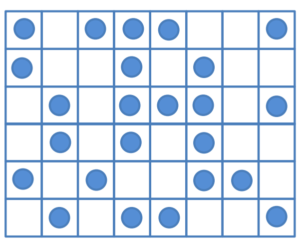
RMS width $\propto \sqrt{N}$

Note also, 4th moment treat in similar way: find ratio of 2nd and 4th moments identical to Gaussian distribution (Bell curve).

Physical examples:

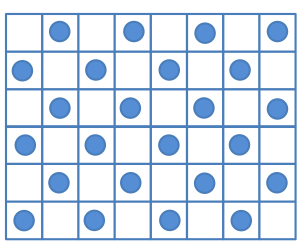


Diffusing atoms randomly located on lattice
≈ 2-state random magnetization problem
(Rough equivalent situation for ideal gas atoms)



If $k_B T >> \Delta U$, larger entropy overwhelmingly favors this configuration
(we will see a more formal way to treat such a fixed temperature case later)

↕ Small ΔU



"Low-T state": Entropy = 0
(e.g. Copper + gold can order this way)

Imbalanced example:

$N_1 = 100$ ⇔ atoms $N_2 = 300$

100 & 300 "bins"

$N = 5$ $N = 15$

20 total atoms, expected location of atoms?

- independent configurations: probabilities <u>multiply</u>.
- peak value based on maximum Ω

In[1]:= $N\left[\frac{100! \times 300!}{5! \times 95! \times 15! \times 285!}\right]$

Out[1]= 5.78801×10^{32}

Maximum <u>entropy</u>

In[2]:= $N\left[\frac{100! \times 300!}{4! \times 96! \times 16! \times 284!}\right]$

Out[2]= 5.36974×10^{32}

In[3]:= $N\left[\frac{100! \times 300!}{6! \times 94! \times 14! \times 286!}\right]$

Out[3]= 4.80648×10^{32}