

# Today

- I. There is class on Monday; Last Time
  - II. The Maxwell-Boltzmann Speed Distribution's Properties
  - III. Zak's Guest Lecture: The Partition Function and the Helmholtz Free Energy
  - IV. Partition Functions of Composite Systems
- I. We derived the Maxwell-Boltzmann speed distribution:

$$\mathcal{D}(v) = \left( \frac{m}{2\pi kT} \right)^{3/2} 4\pi v^2 e^{-mv^2/2kT},$$

we interpret this as a probability density for the speed of a gas molecule in equilibrium at temperature  $T$ .

Recall early on we calculated  $v_{rms} = \sqrt{\frac{3kT}{m}}$

II. We can find the most probable velocity by computing

$\frac{d}{dv} \mathcal{D}(v) = 0$ , which gives  $v_{max} = \sqrt{\frac{2kT}{m}}$ . We can also use this

distribution to find the mean velocity of the gas,

$$\bar{v} = \int_0^{\infty} v \mathcal{D}(v) dv = \sqrt{\frac{8kT}{\pi m}}.$$

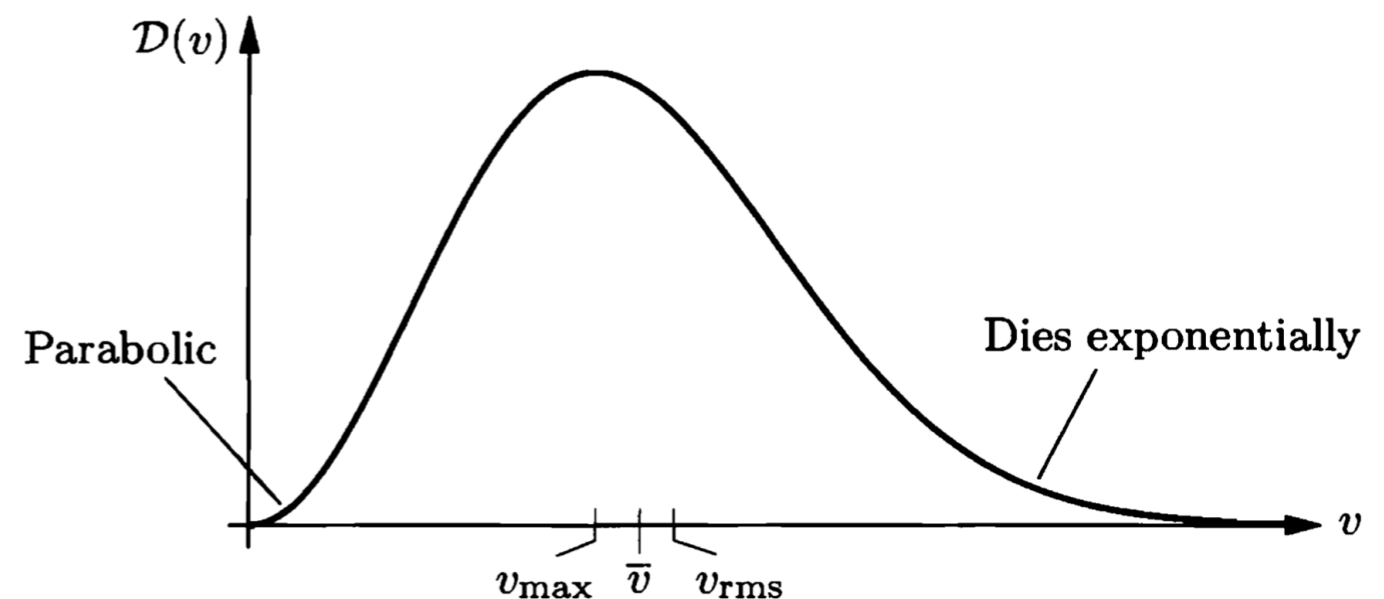
Let's consider the the probability of finding a gas molecule moving faster than the speed of sound. We can compute this as

$$Prob(v > 343 \text{ m/s}) = \int_{343 \text{ m/s}}^{\infty} \mathcal{D}(v) dv = \int_{343 \text{ m/s}}^{\infty} \left( \frac{m}{2\pi kT} \right)^{3/2} 4\pi v^2 e^{-mv^2/2kT} dv$$

Substitute

$$x = \frac{v}{v_{max}},$$

$$Prob = \frac{4}{\sqrt{\pi}} \int_{x_{min}}^{\infty} x^2 e^{-x^2} dx$$



II. Let's consider the the probability of finding a gas molecule moving faster than the speed of sound. We can compute this as

$$Prob(v > 343 \text{ m/s}) = \int_{343 \text{ m/s}}^{\infty} \mathcal{D}(v)dv = \int_{343 \text{ m/s}}^{\infty} \left(\frac{m}{2\pi kT}\right)^{3/2} 4\pi v^2 e^{-mv^2/2kT} dv$$

Substitute

$$x = \frac{v}{v_{max}},$$

$$Prob = \frac{4}{\sqrt{\pi}} \int_{x_{min}}^{\infty} x^2 e^{-x^2} dx$$

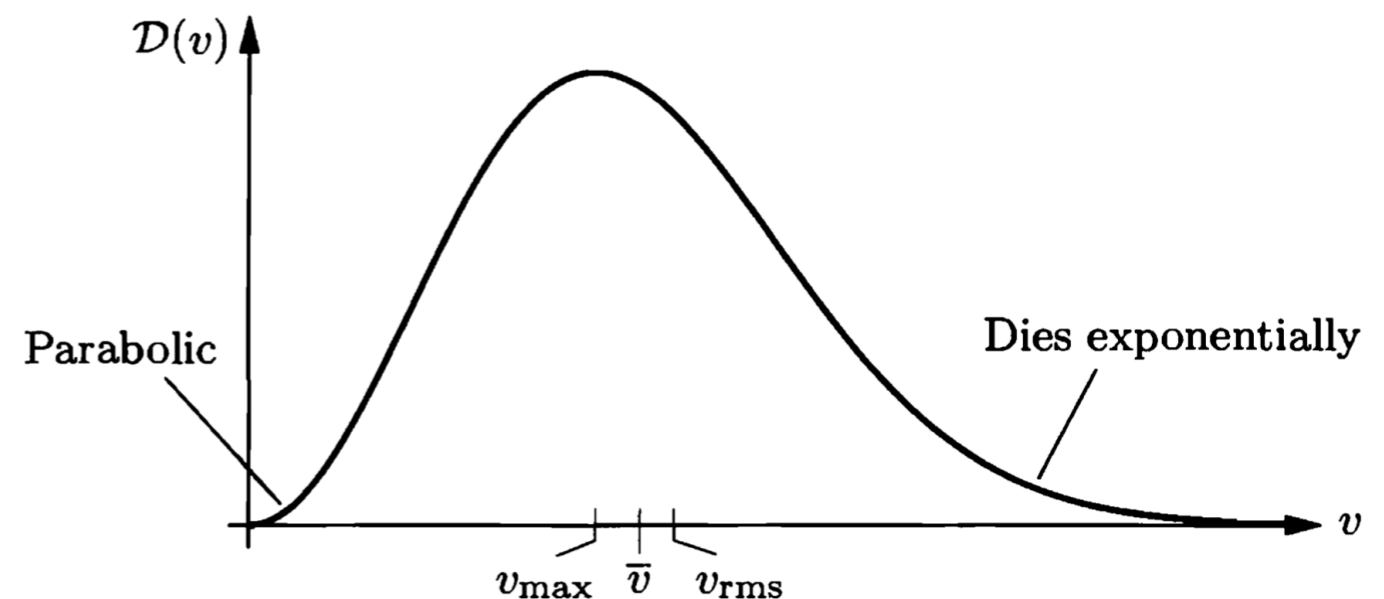
For Nitrogen at room temperature

$$v_{max} = 422 \text{ m/s}$$

$$x_{min} = \frac{343}{422} = 0.81,$$

$$Prob = 0.726.$$

III. See slides from Zak's guest lecture.



IV. Partition function of composite systems. Let's start with just two particles. The total of two interacting particles can be complicated. Instead let's take the two particles to be noninteracting. Then

$$E_{tot} = E_1 + E_2, \text{ and for this case the partition function simplifies}$$
$$Z_{total} = \sum_s e^{-\beta E_{tot}} = \sum_s e^{-\beta(E_1+E_2)} = \sum_s e^{-\beta E_1} e^{-\beta E_2}.$$

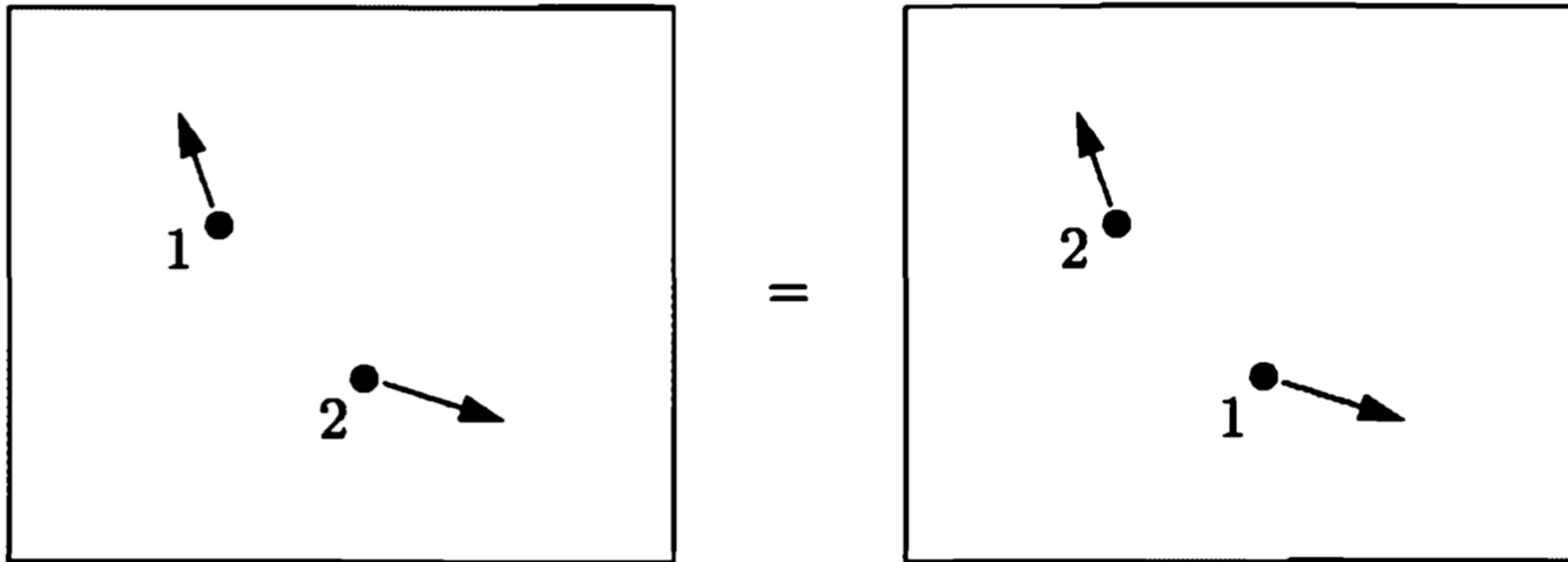
This is still hard to work with, but if we assume the two particles are distinguishable, then we can say that particle 1 is in the state  $s_1$  and that particles is in the state  $s_2$ . That is,  $s = (s_1, s_2)$ , and we have

$$Z_{total} = \sum_{s_1} \sum_{s_2} e^{-\beta E_1(s_1)} e^{-\beta E_2(s_2)} = \sum_{s_1} e^{-\beta E_1(s_1)} \sum_{s_2} e^{-\beta E_2(s_2)} = Z_1 Z_2$$

(noninteracting, distinguishable particles). What if I had  $N$  noninteracting distinguishable particles?

$$Z_{total} = Z_1 Z_2 \cdots Z_N.$$

IV.



For identical particles all I need to do is compensate for over counting,

$$Z_{total} = \frac{1}{2} Z_1 Z_2 = \frac{1}{2} (Z_1)^2.$$

For  $N$  identical particles the over counting is  $N!$ , so we have

$$Z_{total} = \frac{1}{N!} (Z_1)^N \quad (\text{noninteracting, indistinguishable particles}).$$