

# CHEM 26300 (Chemical Kinetics and Dynamics) Notes

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# Chapter 27

## Kinetic Theory of Gases

### 27.1 Background and Ideal Gas Distributions

3/28:

- Learning objectives for CHEM 263.
  - The time-dependent phenomena.
  - Reaction rate and rate laws.
  - Reaction mechanisms and reaction dynamics.
  - Surface chemistry and catalysis.
  - Experimental design and instruments.

- Before we move into the content of CHEM 263, a few important notes from CHEM 262.

- **Partition function** (for a system with  $N$  states): The following function of temperature. *Denoted by  $Q(T)$ . Given by*

$$Q(T) = \sum_{n=1}^N e^{-E_n/k_B T}$$

- **Observable:** A quantum mechanical operator.
- Consider a system described by the partition function  $Q$ . Let  $|i\rangle$  denote the state with energy  $E_i$ , and let  $A$  be an observable. Then the expected value of the observable  $A$  is given by

$$\langle A \rangle = \frac{1}{Q} \sum_{|i\rangle} \langle i|A|i\rangle e^{-E_i/k_B T}$$

- “This fundamental law is the summit of statistical mechanics, and the entire subject is either the slide-down from this summit, as the principle is applied to various cases, or the climb-up to where the fundamental law is derived and the concepts of thermal equilibrium and temperature  $T$  clarified” Richard Feynman, Statistical Mechanics.
- Now onto the CHEM 263 content.
- Tian duplicates the derivation of the ideal gas law given on Labalme (2021b, pp. 18–19).
  - Note that if  $M$  is the molar mass,  $m$  is the mass of a single molecule,  $N_A$  is Avogadro’s number,  $N$  is the number of particles present, and  $n$  is the number of moles present, then since  $N/N_A = n$  and  $M/N_A = m$ , we have that

$$M = \frac{Nm}{n}$$

- Important values of molecular speed  $u$ .

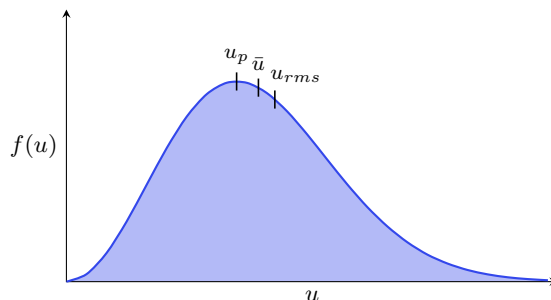


Figure 27.1: Important values of molecular speed.

- **Maxwell Speed Distribution Function:** The following normalized function, which gives the probability that a particle in an ideal gas will have a given speed. Denoted by  $f(u)$ . Given by

$$f(u) = 4\pi \left( \frac{M}{2\pi RT} \right)^{3/2} u^2 \exp \left( -\frac{Mu^2}{2RT} \right)$$

- **Most probable speed:** The speed that a particle in an ideal gas is most likely to have. Denoted by  $u_p$ . Given by

$$u_p = \sqrt{\frac{2RT}{M}}$$

- **Mean speed:** The average speed of all of the particles in an ideal gas. Denoted by  $\bar{u}$ . Given by

$$\bar{u} = \sqrt{\frac{8RT}{\pi M}}$$

- **Root mean squared speed:** The square root of the average of the speeds squared. Denoted by  $u_{rms}$ . Given by

$$u_{rms} = \langle u^2 \rangle^{1/2} = \sqrt{\frac{3RT}{M}}$$

- The distributions of the molecular speed and velocity components are different.
  - While speed follows the Maxwell-Boltzmann distribution, velocity follows (on each Cartesian axis) a Gaussian distribution centered at zero.
  - At higher temperatures, both distributions “flatten out,” but maintain their shape.
- Deriving the distribution of the velocity component.
  - The velocity components are independent.
  - Let

$$h(u) = h(u_x, u_y, u_z) = f(u_x)f(u_y)f(u_z)$$

be the distribution of speed with velocity components between  $u_x, u_x + du_x$ ,  $u_y, u_y + du_y$ , and  $u_z, u_z + du_z$ , where  $f(u_i)$  is the probability distribution of components  $i$ .

- Note that  $h(u)$  is *not* the speed distribution with velocity components between  $u, u + du$ .
- Clever step: Note that the logarithmic form of the above equation leads to

$$\begin{aligned} \ln h(u) &= \ln f(u_x) + \ln f(u_y) + \ln f(u_z) \\ \left( \frac{\partial \ln h}{\partial u_x} \right)_{u_y, u_z} &= \frac{d \ln h}{du} \left( \frac{\partial u}{\partial u_x} \right)_{u_y, u_z} \\ &= \frac{u_x}{u} \frac{d \ln h}{du} \end{aligned}$$

where we evaluate  $\partial u / \partial u_x$  by using the generalized Pythagorean theorem definition of  $u$ .

- Additionally, we have that

$$\left( \frac{\partial \ln h}{\partial u_x} \right)_{u_y, u_z} = \frac{d \ln f(u_x)}{du_x}$$

since the  $\ln f(u_i)$  ( $i \neq x$ ) terms are constant with respect to changes in  $u_x$ .

- Thus, combining the last two results, we have that

$$\frac{d \ln h(u)}{u du} = \frac{d \ln f(u_x)}{u_x du_x}$$

- It follows since the gas is isotropic that

$$\frac{d \ln h(u)}{u du} = \frac{d \ln f(u_x)}{u_x du_x} = \frac{d \ln f(u_y)}{u_y du_y} = \frac{d \ln f(u_z)}{u_z du_z}$$

- But since the three speed components are independent of each other, the above term is constant.
- It follows if we call the constant  $-2\gamma$ , then

$$\begin{aligned} \frac{d \ln f(u_i)}{u_i du_i} &= -2\gamma \\ f(u_i) &= A e^{-\gamma u_i^2} \end{aligned}$$

for  $i = x, y, z$ .

- We will pick up with solving for  $A$  and  $\gamma$  in the next lecture.

## 27.2 Velocity vs. Speed

3/30:

- Exam preferences.
  - Asks for midterm preferences. People prefer a take-home exam.
  - Asks for final preferences. Probably a 2-hour test?
- Continuing with the derivation for the distribution of the velocity component.
  - Note that we choose  $-2\gamma$  because we know we're gonna have to integrate and we want the final form to be as simple as possible. For instance,

$$\frac{d \ln f(u_i)}{u_i du_i} = \frac{d \ln f(u_i)}{\frac{1}{2} du_i^2}$$

should help rationalize the 2.

- Solving for  $A$ .
  - We apply the normalization requirement.

$$\begin{aligned} 1 &= \int_{-\infty}^{\infty} f(u_i) du_i \\ &= A \int_{-\infty}^{\infty} e^{-\gamma u_i^2} du_i \\ &= 2A \int_0^{\infty} e^{-\gamma u_i^2} du_i \\ &= 2A \sqrt{\frac{\pi}{4\gamma}} \\ A &= \sqrt{\frac{\gamma}{\pi}} \end{aligned}$$

- Thus, for  $i = x, y, z$ , we have

$$f(u_i) = \sqrt{\frac{\gamma}{\pi}} e^{-\gamma u_i^2}$$

- Solving for  $\gamma$ .

- We know from the previous lecture that

$$\begin{aligned} \frac{1}{3} m \langle u^2 \rangle &= RT \\ \langle u^2 \rangle &= \frac{3RT}{M} = \frac{3k_B T}{m} \\ \langle u_x^2 \rangle &= \frac{RT}{M} \end{aligned}$$

- But we also have by definition that (taking  $u_x$  in particular because  $\gamma$  is the same in the equations for  $u_x, u_y, u_z$ )

$$\langle u_x^2 \rangle = \int_{-\infty}^{\infty} u_x^2 f(u_x) du_x$$

- Thus, we have that

$$\begin{aligned} \frac{RT}{M} &= \int_{-\infty}^{\infty} u_x^2 f(u_x) du_x \\ &= \sqrt{\frac{\gamma}{\pi}} \int_{-\infty}^{\infty} u_x^2 e^{-\gamma u_x^2} du_x \\ &= 2\sqrt{\frac{\gamma}{\pi}} \int_0^{\infty} u_x^2 e^{-\gamma u_x^2} du_x \\ &= 2\sqrt{\frac{\gamma}{\pi}} \cdot \frac{1}{4\gamma} \sqrt{\frac{\pi}{\gamma}} \\ &= \frac{1}{2\gamma} \\ \gamma &= \frac{M}{2RT} \end{aligned}$$

- It follows that

$$f(u_i) = \sqrt{\frac{M}{2\pi RT}} e^{-Mu_i^2/2RT} = \sqrt{\frac{m}{2\pi k_B T}} e^{-mu_i^2/2k_B T}$$

- Now we can compute other speeds, such as the average velocity  $\langle u_x \rangle$ .
  - Evaluating the odd integrand gives us  $\langle u_x \rangle = 0$ , as expected.
- As per the Gaussian distribution, if the temperature increases or mass decreases, the distribution of speeds broadens and flattens.
- **Doppler effect:** The change in frequency of a wave in relation to an observer who is moving relative to the wave source. *Also known as Doppler shift.*
  - Example: The change of pitch heard when a vehicle sounding a horn approaches and recedes from an observer. Compared to the emitted frequency, the received frequency is higher during the approach, identical at the instant of passing by, and lower during the recession.
- An application of the velocity distribution: The Doppler effect and spectral line broadening.
  - Radiation emitted from a gas will be spread out due to the motion of the molecules.
  - The frequency  $\nu$  detected by the observer and the frequency  $\nu_0$  emitted by the emitter are related by

$$\nu \approx \nu_0 \left( 1 + \frac{u_x}{c} \right)$$

- Algebraic rearrangement gives us

$$u_x = \frac{c(\nu - \nu_0)}{\nu_0}$$

- Doppler-broadened spectral lineshape.

$$I(\nu) \propto e^{-mc^2(\nu - \nu_0)^2 / 2\nu_0 k_B T}$$

- Thus, the variance of the spectral line is

$$\sigma^2 = \frac{\nu_0^2 k_B T}{mc^2} = \frac{\nu_0^2 RT}{Mc^2}$$

- The result is that if gas particles are at rest, the emission line spectrum will have very narrow lines. If the gas particles are moving, the lines are broadened.

■ This is why so much spectroscopy is done at super-low temperatures and with heavier molecules! In particular, because Doppler broadening blurs results.

- We know that the average velocity is zero. But we can also consider the average velocity in the positive direction.

- We calculate

$$\begin{aligned} \langle u_x \rangle &= \int_0^\infty u_x f(u_x) du_x \\ &= \sqrt{\frac{m}{2\pi k_B T}} \int_0^\infty u_x e^{-mu_x^2 / 2k_B T} \\ &= \sqrt{\frac{m}{2\pi k_B T}} \cdot \frac{2k_B T}{2m} \\ &= \sqrt{\frac{m}{2\pi k_B T}} \end{aligned}$$

- This will be one-fourth the average speed from Figure 27.1, though.

- Moving from velocity to speed: Deriving the Maxwell-Boltzmann Speed Distribution.

- Define

$$F(u) du \approx f(u_x) du_x f(u_y) du_y f(u_z) du_z$$

■ This function gives us the velocity of each particle in the velocity space. But the speed of each particle is just it's distance from the origin.

- We have that

$$F(u) du \approx \left( \frac{m}{2\pi k_B T} \right)^{3/2} e^{-m(u_x^2 + u_y^2 + u_z^2) / 2k_B T} du_x du_y du_z$$

from where we can convert to spherical coordinates using  $u^2 = u_x^2 + u_y^2 + u_z^2$  and  $4\pi u^2 du = du_x du_y du_z$  to get our final result.

$$F(u) du = 4\pi \left( \frac{m}{2\pi k_B T} \right)^{3/2} u^2 e^{-mu^2 / 2k_B T} du$$

- Note that we invoke the equals sign only at the end because speed is inherently spherical in the velocity space; any use of Cartesian infinitesimals must by definition be an approximation at best.

- Some important differences.



- $h(u) = h(u_x, u_y, u_z) = f(u_x)f(u_y)f(u_z)$  is the distribution of molecular speeds with velocity components (in Cartesian coordinates) between  $u_x, u_x + du_x$ ,  $u_y, u_y + du_y$ , and  $u_z, u_z + du_z$ .
- $f(u_x) = \sqrt{M/2\pi RT} e^{-Mu_x^2/2RT}$  is the distribution of molecular speed componentwise in Cartesian coordinates, and has a Gaussian distribution.
- $F(u) = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} u^2 e^{-mu^2/2k_B T}$  is the distribution of molecular speed, and has a Maxwell-Boltzmann distribution as per spherical coordinates.
- Maxwell-Boltzmann speed distribution of noble gases.
  - Heavier Noble gases have more “flattened” M-B distributions.
- Different metrics of M-B speed distribution.
  - We can, from the above formula, calculate the average speed  $\langle u \rangle$ , the root mean square speed  $\langle u^2 \rangle$ , and the most probable speed by taking a derivative and setting it equal to zero.
  - We get

$$\langle u \rangle = \sqrt{\frac{8RT}{\pi M}} \qquad \langle u^2 \rangle = \sqrt{\frac{3RT}{M}} \qquad u_{\text{mp}} = \sqrt{\frac{2k_B T}{m}}$$

## 27.3 Chapter 27: The Kinetic Theory of Gases

From McQuarrie and Simon (1997).

- 3/28:
- **Kinetic theory of gases:** A simple model of gases in which the molecules (pictured as hard spheres) are assumed to be in constant, incessant motion, colliding with each other and with the walls of the container.
  - McQuarrie and Simon (1997) does the KMT derivation of the ideal gas law from Labalme (2021a). Some important notes follow.
    - McQuarrie and Simon (1997) emphasizes the importance of

$$PV = \frac{1}{3}Nm \langle u^2 \rangle$$

as a fundamental equation of KMT, as it relates a macroscopic property  $PV$  to a microscopic property  $m \langle u^2 \rangle$ .

- In Chapter 17-18, we derived quantum mechanically, and then from the partition function, that the average translational energy  $\langle E_{\text{trans}} \rangle$  for a single particle of an ideal gas is  $\frac{3}{2}k_B T$ . From classical mechanics, we also have that  $\langle E_{\text{trans}} \rangle = \frac{1}{2}m \langle u^2 \rangle$ . *This* is why we may let

$$\frac{1}{2}m \langle u^2 \rangle = \frac{3}{2}k_B T$$

recovering that the average translational kinetic energy of the molecules in a gas is directly proportional to the Kelvin temperature.

- **Isotropic** (entity): An object or substance that has the same properties in any direction.
  - For example, a homogeneous gas is isotropic, and this is what allows us to state that  $\langle u_x^2 \rangle = \langle u_y^2 \rangle = \langle u_z^2 \rangle$ .
- McQuarrie and Simon (1997) derives

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

- $u_{\text{rms}}$  is an estimate of the average speed since  $\langle u^2 \rangle \neq \langle u \rangle^2$  in general.
- McQuarrie and Simon (1997) states without proof that the speed of sound  $u_{\text{sound}}$  in a monatomic ideal gas is given by

$$u_{\text{sound}} = \sqrt{\frac{5RT}{3M}}$$

- Assumptions of the kinetic theory of gases.
  - Particles collide elastically with the wall.
    - Justified because although each collision will not be elastic (the particles in the wall are moving too), the average collision will be elastic.
  - Particles do not collide with each other.
    - Justified because “if the gas is in equilibrium, on the average, any collision that deflects the path of a molecule... will be balanced by a collision that replaces the molecule” (McQuarrie & Simon, 1997, p. 1015).
- Note that we can do the kinetic derivation at many levels of rigor, but more rigorous derivations offer results that differ only by constant factors on the order of unity.
- Deriving a theoretical equation for the distribution of the *components* of molecular velocities.
  - Let  $h(u_x, u_y, u_z) du_x du_y du_z$  be the fraction of molecules with velocity components between  $u_j$  and  $u_j + du_j$  for  $j = x, y, z$ .
  - Assume that the each component of the velocity of a molecule is independent of the values of the other two components<sup>1</sup>. It follows statistically that

$$h(u_x, u_y, u_z) = f(u_x)f(u_y)f(u_z)$$

- Note that we use just one function  $f$  for the probability distribution in each direction because the gas is isotropic.
- We can use the isotropic condition to an even greater degree. Indeed, it implies that any information conveyed by  $u_x$  is necessarily and sufficiently conveyed by  $u_y$ ,  $u_z$ , and  $u$ . Thus, we may take

$$h(u) = h(u_x, u_y, u_z) = f(u_x)f(u_y)f(u_z)$$

- It follows that

$$\frac{\partial \ln h(u)}{\partial u_x} = \frac{\partial}{\partial u_x} (\ln f(u_x) + \text{terms not involving } u_x) = \frac{d \ln f(u_x)}{du_x}$$

- Since

$$\begin{aligned} u^2 &= u_x^2 + u_y^2 + u_z^2 \\ \frac{\partial}{\partial u_x}(u^2) &= \frac{\partial}{\partial u_x}(u_x^2 + u_y^2 + u_z^2) \\ 2u \frac{\partial u}{\partial u_x} &= 2u_x \\ \frac{\partial u}{\partial u_x} &= \frac{u_x}{u} \end{aligned}$$

we have that

$$\begin{aligned} \frac{\partial \ln h}{\partial u_x} &= \frac{d \ln h}{du} \frac{\partial u}{\partial u_x} = \frac{u_x}{u} \frac{d \ln h}{du} \\ \frac{d \ln h(u)}{u du} &= \frac{d \ln f(u_x)}{u_x du_x} \end{aligned}$$

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<sup>1</sup>This can be proven.

which generalizes to

$$\frac{d \ln h(u)}{u \, du} = \frac{d \ln f(u_x)}{u_x \, du_x} = \frac{d \ln f(u_y)}{u_y \, du_y} = \frac{d \ln f(u_z)}{u_z \, du_z}$$

- Since  $u_x, u_y, u_z$  are independent, we know that the above equation is equal to a constant, which we may call  $-\gamma$ . It follows that for any  $j = x, y, z$ , we have that

$$\begin{aligned} \frac{d \ln f(u_j)}{u_j \, du_j} &= -\gamma \\ \frac{1}{f} \frac{df}{du_j} &= -\gamma u_j \\ \int \frac{df}{f} &= \int -\gamma u_j \, du_j \\ \ln f &= -\frac{\gamma}{2} u_j^2 + C \\ f(u_j) &= A e^{-\gamma u_j^2} \end{aligned}$$

where we have incorporated the  $1/2$  into  $\gamma$ .

- To determine  $A$  and  $\gamma$ , we let arbitrarily let  $j = x$ . Since  $f$  is a continuous probability distribution, we may apply the normalization requirement.

$$\begin{aligned} 1 &= \int_{-\infty}^{\infty} f(u_x) \, du_x \\ &= 2A \int_0^{\infty} e^{-\gamma u_x^2} \, du_x \\ &= 2A \sqrt{\frac{\pi}{4\gamma}} \\ A &= \sqrt{\frac{\gamma}{\pi}} \end{aligned}$$

- Additionally, since we have that  $\langle u_x^2 \rangle = \frac{1}{3} \langle u^2 \rangle$  and  $\langle u^2 \rangle = 3RT/M$ , we know that  $\langle u_x^2 \rangle = RT/M$ . This combined with the definition of  $\langle u_x^2 \rangle$  as a continuous probability distribution yields

$$\begin{aligned} \frac{RT}{M} &= \langle u_x^2 \rangle \\ &= \int_{-\infty}^{\infty} u_x^2 f(u_x) \, du_x \\ &= 2 \sqrt{\frac{\gamma}{\pi}} \int_0^{\infty} u_x^2 e^{-\gamma u_x^2} \, du_x \\ &= 2 \sqrt{\frac{\gamma}{\pi}} \cdot \frac{1}{4\gamma} \sqrt{\frac{\pi}{\gamma}} \\ &= \frac{1}{2\gamma} \\ \gamma &= \frac{M}{2RT} \end{aligned}$$

- Therefore,

$$f(u_x) = \sqrt{\frac{M}{2\pi RT}} e^{-Mu_x^2/2RT}$$

- It is common to rewrite the above in terms of molecular quantities  $m$  and  $k_B$ .

- It follows that as temperature increases, more molecules are likely to be found with higher component velocity values.
- We can use the above result to show that

$$\langle u_x \rangle = \int_{-\infty}^{\infty} u_x f(u_x) du_x = 0$$

- We can also calculate that  $\langle u_x^2 \rangle = RT/M$  and  $m \langle u_x^2 \rangle / 2 = k_B T / 2$  from the above result<sup>[2]</sup>.
  - An important consequence is that the total kinetic energy is divided equally into the  $x$ -,  $y$ -, and  $z$ -components. This fact was also demonstrated in Week 1, Lecture 3.
- **Doppler broadening:** The broadening of spectral lines due to the distribution of molecular velocities.
  - Ideally, spectral lines will be very narrow.
  - However, due to the Doppler effect, if an atom or molecule emits radiation of frequency  $\nu_0$  while moving away or toward the observer with speed  $u_x$ , then the observed frequency will be

$$\nu \approx \nu_0 \left( 1 + \frac{u_x}{c} \right)$$

- Indeed, “if one observes the radiation emitted from a gas at temperature  $T$ , then it is found that the spectral line at  $\nu_0$  will be spread out by the Maxwell distribution of  $u_x$  of the molecule emitting the radiation” (McQuarrie & Simon, 1997, p. 1021).
- It follows by the definition of  $f(u_x)$  and the above that

$$I(\nu) \propto e^{-mc^2(\nu-\nu_0)^2/2\nu_0^2k_B T}$$

i.e., that  $I(\nu)$  is of the form of a Gaussian centered at  $\nu_0$  with variance  $\sigma^2 = \nu_0^2 k_B T / mc^2$ .

- Deriving **Maxwell-Boltzmann distribution**.
  - Let the probability that a molecule has speed between  $u$  and  $u + du$  be defined by a continuous probability distribution  $F(u) du$ . In particular, we have from the above isotropic condition that

$$\begin{aligned} F(u) du &= f(u_x) du_x f(u_y) du_y f(u_z) du_z \\ &= \left( \frac{m}{2\pi k_B T} \right)^{3/2} e^{-m(u_x^2 + u_y^2 + u_z^2)/2k_B T} du_x du_y du_z \end{aligned}$$

- Considering  $F$  over a **velocity space**, we realize that we may express the probability distribution  $F$  as a function of  $u$  via  $u^2 = u_x^2 + u_y^2 + u_z^2$  and the differential volume element in every direction over the sphere of equal velocities (a sphere by the isotropic condition) by  $4\pi u^2 du = du_x du_y du_z$ .
- Thus, the Maxwell-Boltzmann distribution in terms of speed is

$$F(u) du = 4\pi \left( \frac{m}{2\pi k_B T} \right)^{3/2} u^2 e^{-mu^2/2k_B T} du$$

- **Maxwell-Boltzmann distribution:** The distribution of molecular speeds.
- **Velocity space:** A rectangular coordinate system in which the distances along the axes are  $u_x, u_y, u_z$ .
- We may use the above result to calculate that

$$\langle u \rangle = \sqrt{\frac{8RT}{\pi m}}$$

which only differs from  $u_{\text{rms}}$  by a factor of 0.92.

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<sup>2</sup>See the equipartition of energy theorem from Labalme (2021b).

- **Most probable speed:** The most probable speed of a gas molecule in a sample that obeys the Maxwell-Boltzmann distribution. *Denoted by  $u_{\text{mp}}$ . Given by*

$$u_{\text{mp}} = \sqrt{\frac{2RT}{M}}$$

– Derived by setting  $dF/du = 0$ .

- We may also express the Maxwell-Boltzmann distribution in terms of energy via  $u = \sqrt{2\varepsilon/m}$  and  $du = d\varepsilon/\sqrt{2m\varepsilon}$  to give

$$F(\varepsilon) d\varepsilon = \frac{2\pi}{(\pi k_B T)^{3/2}} \sqrt{\varepsilon} e^{-\varepsilon/k_B T} d\varepsilon$$

- We can also confirm our previously calculated values for  $\langle u^2 \rangle$  and  $\langle \varepsilon \rangle$ .
- McQuarrie and Simon (1997) does a higher-level derivation of the ideal gas law that is rather analogous to the one done in class (i.e., via its flux perspective).
- McQuarrie and Simon (1997) discusses a simple and Nobel-prize winning experiment that verified the Maxwell-Boltzmann distribution.

# References

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