## Lecture 07: Statistical Physics of the Ideal Gas

In these notes we derive the partition function for a gas of non-interacting particles in a fixed volume.

# 1   Particles in a room

One of the motivations in developing a formulation of equilibrium statistical physics grounded in the properties of the microstate rather than the properties of the macrostate was that we wanted to be able to determine the velocity distribution of particles in a classroom. With the work done in our previous notes we are now in a position to achieve this objective plus some others concerning point particles moving in free space. This discussion will introduce us to the **ideal gas model** and will in turn allow us to derive the eponymous law governing how pressure, volume, temperature, and number of particles of a gas are related to one another. A schematic of the system we will be analyzing is shown in Fig. 1.
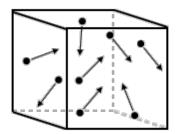


Figure 1: In these notes we will be studying a system of $N$ mobile particles confined to a volume $V$ and at a temperature $T$.

In the ideal gas model, we represent the molecules or atoms that make up a gas as point particles confined to a fixed volume and at a thermal equilibrium. As we build up this model, we can use a number of framing questions as guides

**Framing Questions**
What is the partition function for the system shown in Fig. 1? What is the probability distribution of speeds for air particles in a room? How do pressure, volume, temperature, and number of particles of a gas relate to one another?

# 2   Partition Function of an Ideal Gas

Determining the distribution of speeds of gas molecules in a fixed volume amounts to determining the probability distribution for the particle to be in a particular in a particular microstate of the system. By our discussion in Lecture Notes 06 ”Boltzmann Distribution and Partition Function”, determining the probability to be in a particular microstate involves computing the partition function for the system. However, before we attempt to calculate the partition function, we will make a number of simplifying assumptions about this system.

First, although the molecules of air consist of a combination of various **noble gases** of the periodic table all of which have different masses, we will assume all $N$ particles in the volume $V$ have the common mass $m$ and that all the particles are identical. Also, although many gas molecules have shapes different from point particles (e.g., $H_2$, $N_2$, and $O_2$ all look like dumbbells), we will assume all gas particles are point particles. Finally, in real gases, the particles interact (albeit weakly) with one another, but for the ideal gas we will assume the particles do not interact with one another. Listed in full, the approximations are

– Same mass for all particles and particles are identical

– All particles are point particles

– Particles are non-interacting

These assumptions constitute the **ideal gas approximation** for gaseous particles. They may seem somewhat over-generous and hence unphysical, but they capture quite well many of the important properties (like speed distributions!) of real gases.

Now, our goal is to compute the partition function for the ideal gas. Knowing the partition function allows us to find the probability to be in various microstates of the system. We previously found that the general expression for the partition function of a system is

$$Z = \sum_{\{i\}} e^{-\beta E_i}, \tag{1}$$

where $i$ denotes a particular microstate of the system, $E_i$ is the energy of the microstate, and $\sum_{\{i\}}$ is a summation over all microstates. Therefore in order to compute the partition function for an ideal gas, we need to

1. Define the microstate for the system

2. Determine the energy of a microstate

3. Define the summation over microstates

We tackle each of these tasks in turn.

1. **Definition of a microstate**

    We have $N$ particles in a volume $V$. These particles are all in a great deal of motion, zooming past one another, colliding with the walls of the volume, and then rebounding off in some new direction. What could the microstate of such a system possibly be (not to mention the collection of all microstates)?

    In answering this question it will first prove useful to recall that a microstates amounts to the most complete description of a system at a given time. Since we are dealing with non-interacting particles, we can begin by considering a single particle with no forces acting on it. Let's say we are considering the particle at a specific point in time. What information do we need in order to completely determine the subsequent motion of the particle?

    From classical mechanics, we know we need to know at least one piece of information: the position of the particle. Let us denote the position of the particle by a vector $\mathbf{q}$ in three dimensions. In component form, we have $\mathbf{q} = (x, y, z)$. If we knew that the particle was in position $\mathbf{q}$, would we then have a complete description of the particle's state? No; knowing only the position of the particle amounts to knowing where the particle is but not *where it is going*. The particle might be in a specific location, but it could be traveling in any direction, so knowing the position alone is not enough to specify the state of the particle.

Now, let's say we knew the momentum of the particle[1]. We denote the momentum by the vector **p** which, in three dimensions, has the component form $\mathbf{p} = (p_x, p_y, p_z)$. Knowing the momentum of the particle (and knowing the mass), we then know direction the particle is moving and how fast its moving. But, if we only knew the momentum, we would not know where the particle is. It could be starting from any position in the volume $V$.

Therefore, in order to specify the state of the particle, we need to know where the particle is, where it is going, and how fast it is going there. The first piece of information is given by the position vector **q**, and the last two pieces of information are given by the momentum vector **p**. Therefore, for a single particle the microstate is defined by **q** and **p**. The microstate for a system of $N$ particles is easy to extrapolate:

> **Microstate for $N$ particles:** A microstate for our system of $N$ particles in three-dimensions is defined by $\mathbf{q}_1, \mathbf{p}_1, \mathbf{q}_2, \mathbf{p}_2, \ldots, \mathbf{q}_N, \mathbf{p}_N$ where $\mathbf{q}_i, \mathbf{p}_i$ are the position and momentum vectors, respectively, of the particle $i$.

2. **Energy of a microstate**

We have a collection of $N$ non-interacting particles confined within a volume $V$. These particles are free (i.e., there are no forces acting on them) and, at one point in time, are in the microstate $\{\mathbf{q}_1, \mathbf{p}_1, \mathbf{q}_2, \mathbf{p}_2, \ldots, \mathbf{q}_N, \mathbf{p}_N\}$. What is the total energy of all the particles given this microstate?

If no forces are acting on the particles, then the particles do not lose or gain energy as they change position. Therefore, there is no potential energy in the system and all of the energy is kinetic. For the $k$th particle of mass $m$ moving in three dimensions with momentum $\mathbf{p}_k$, the kinetic energy is $\mathbf{p}_k^2/2m$. We can sum all the kinetic energies of this form to determine the total energy of our system. Ultimately, we find that the total energy for our $N$ particle system of free and non-interacting particles is

$$E\left(\{\mathbf{q}_i, \mathbf{p}_i\}\right) = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m}. \tag{2}$$

3. **Summation over microstates**

We have almost assembled all the pieces needed to compute the partition function of the ideal gas. The only thing remaining is determining the appropriate summation over our microstates.

The first thing to note is that our microstate is defined by the continuous variables position and momentum and, consequently, in order to sum over these microstates we need to replace the discrete summation with a continuous integral (or rather, *many* continuous integrals). We must sum over all possible positions the particles can be in and all possible momenta the particles can have, while taking into account the three coordinate directions. Defining this continuous summation is simpler than it seem, as long as we break the calculation down into parts. Since the momentum and position variables are independent, we can independently define the summations over these sets of coordinates.

- **Position Summation**

    Our objective is to define the summation over the possible position microstates of all the particles. In defining this summation we will have to make one assumption that we will further explain later. We assume that each particle can occupy in space a small cube of side length $\delta x$ and volume $(\delta x)^3$. This assumption allows us to break up our larger volume $V$ into a countable collection of smaller volumes. If we allow each particle to occupy any smaller cube in this space, then each particle can be in one of $V/(\delta x)^3$ position microstates. Considering all $N$ particles

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[1]We could just as well use the velocity since the two only differ by a multiplicative constant, but we use momentum for quantum mechanical reasons we will discuss later.

(and allowing particles to occupy the same position microstate), the total number of position microstates for the system is

$$\text{Number of position microstates} = \left( \frac{V}{(\delta x)^3} \right)^N = \frac{V^N}{(\delta x)^{3N}}. \tag{3}$$

Eq.(3) gives us the number of position microstates for our $N$ particle system, but it does not exactly tell us how to *sum* over position microstates. It turns out that, for this system, since the energy of a microstate (given by Eq.(2)) is position independent, we actually don't need to define a summation over position microstates; we can just calculate the total number of microstates directly. But in preparation for the momentum summation, we can, as practice, define Eq.(3) as a summation over positions.

We define the volume $V$ that the particles can occupy as the three dimensional integral

$$V \equiv \int_V d^3\mathbf{q} = \iiint_V dx\, dy\, dz. \tag{4}$$

For example, the volume $V$ can be the volume of a box of side length $L$ and each of the integrations in the last equality of Eq.(4) can run from $0$ to $L$. Noting that Eq.(4) could define the volume for any coordinate $\mathbf{q}_k$ for a particle $k$, we extrapolate from Eq.(3) and say the summation over position microstates is given by

$$\text{Summation over position microstates} = \frac{1}{(\delta x)^{3N}} \int_V d^3\mathbf{q}_1 \cdots \iiint_V d^3\mathbf{q}_N. \tag{5}$$

What remains to be discussed is the meaning of $(\delta x)^3$. But first we discuss the summation over momenta.

- **Momentum Summation**

    The summation over the momenta of the particles can be built up analogously to the summation over positions. However, since the momenta are not confined to be within a specific domain in the way that the positions are, we need to sum over *all* of momentum space and not just momenta confined to some abstract cube. That is, we sum each momentum coordinate for each particle from $-\infty$ to $+\infty$. To "count" the microstates in this summation, we break momentum space up into a lattice of small cubes of side length $\delta p$, and volume $(\delta p)^3$. Thus analogously to Eq.(5), we have

$$\text{Summation over momentum microstates} = \frac{1}{(\delta p)^{3N}} \int_{\text{all } \mathbf{p}} d^3\mathbf{p}_1 \cdots \iiint_{\text{all } \mathbf{p}} d^3\mathbf{p}_N. \tag{6}$$

- **Combinatorial Correction**

    So far we have that the summation over momenta and position is apparently given by

$$\text{Summation over positions and momenta} \overset{?}{=} \frac{1}{(\delta x \delta p)^{3N}} \int d^3\mathbf{q}_1\, d^3\mathbf{p}_1 \cdots \iiint d^3\mathbf{q}_N\, d^3\mathbf{p}_N. \tag{7}$$

Since a microstate of our $N$ particle system is specified by the the collection of coordinates $\mathbf{q}_1, \mathbf{p}_1, \mathbf{q}_2, \mathbf{p}_2, \ldots, \mathbf{q}_N, \mathbf{p}_N$ where $\mathbf{q}_k, \mathbf{p}_k$ are the position and momentum of the $k$th particle, Eq.(7) represents the number of possible microstates in our system. However, because our particles are identical, Eq.(7) actually overcounts the number of microstates.

For example, suppose we had a system with $M$ lattice sites where each lattice site represents a microstate of the system. If we placed two identical particles in this system, then there would be "$M$ choose 2" ways to place the particles among the lattice sites. Moreover for $M \gg 1$, this

quantity could be taken to be $M^2/2$. Similarly, if we place $N$ identical particles amongst the $M$ lattice sites, the number of microstates would be

$$\text{Number of microstates} = \binom{M}{N} \left(= \frac{M!}{N!(M-N)!} \right. \tag{8}$$

Now, for the case where $M \gg N$, we can make the approximation

$$\frac{M!}{(M-N)!} = M(M-1)\cdots(M-(N+1)) \simeq M^N, \tag{9}$$

which allows us take Eq.(8) to be

$$\text{Number of microstates} \simeq \frac{M^N}{N!}. \tag{10}$$

We apply the same reasoning to define the summation over the microstates for our gaseous system. Since Eq.(7) represents the summation over position and momenta, it is analogous to $M$ in the above example. For this summation, the cube dimensions, $\delta x$ and $\delta p$ in position and momentum space respectively, are such that the summation in Eq.(7) is always many orders of magnitude greater than the number of particles. Therefore, the combinatorial-corrected summation over microstates is

$$\text{Sum over positions and momenta} = \frac{1}{N!(\delta x \delta p)^{3N}} \int_V d^3\mathbf{q}_1 \iint_{\text{all } \mathbf{p}} d^3\mathbf{p}_1 \cdots \int_V d^3\mathbf{q}_N \iint_{\text{all } \mathbf{p}} d^3\mathbf{p}_N. \tag{11}$$

In Eq.(11), we converted the approximate result Eq.(10) into an exact equality under the assumption that the errors in the approximation do not affect the final calculation of the partition function. This turns out to be a valid assumption (although it takes some work to show this).

- **Lattice Spacing and Heisenberg Uncertainty**

    With Eq.(11), the only task that remains in defining the summation over microstates is to more precisely define $\delta x$ and $\delta p$. By quantum mechanics, the position and momentum "lattice spacing" $\delta x$ and $\delta p$, respectively, obey the approximate relation $\delta x \delta p \sim h$ where $h$ is known as **Planck's constant**. Planck's constant has units of kg·m$^2$/s or J·s and it has the value $h = 6.626 \times 10^{-34}$ J·s. In quantum mechanics, $\delta x$ and $\delta p$ are the standard deviations in the position and momentum of a particle, and the approximate relation $\delta x \delta p \sim h$ refers to the inability to precisely specify both the position and momentum. More precisely, the expression is written as

$$\delta x \delta p \geq h/4\pi \tag{12}$$

and is known as **Heisenberg's uncertainty principle**.

    A full understanding of the exact statement of the uncertainty principle requires quantum mechanics. For our purposes, we can focus on the approximate form of the expression and take it to define the product of our $\delta x$ and $\delta p$ lattice spacing:

$$\delta x \delta p = h. \qquad \text{[Lattice spacing definition]} \tag{13}$$

    Using Eq.(13) may seem sloppy given the exact statement of the Heisenberg uncertainty principle in Eq.(12). However, remaining within the realm of classical physics, we can see Eq.(13) as an assumption about the sizes of our previously defined $\delta x$ and $\delta p$ cubes, an assumption which can be used to make predictions that allow us to then check the assumption. In other words, if Eq.(13) seems arbitrary, you can just take it as a premise and use the consequences of this premise to determine the premise's validity. We ultimately find that physical predictions in the ideal gas

model are independent of this exact lattice space.

We are at last ready to combine our summations over position and momentum space in order to define the full summation over the microstates of our system. Combining Eq.(7) and Eq.(13), we find

$$\text{Sum over positions and momenta} = \frac{1}{N!h^{3N}} \int_V d^3\mathbf{q}_1 \iint_{\text{all }\mathbf{p}} d^3\mathbf{p}_1 \cdots \int_V d^3\mathbf{q}_N \iint_{\text{all }\mathbf{p}} d^3\mathbf{p}_N \tag{14}$$

## 2.1   Assembling and Evaluating the Partition Function

With an account of how to specify the microstates of this system, the energy of the microstates, and how to perform the summation over these microstates, we are at last prepared to write down the partition function for our ideal gas. The general expression for the partition function of a system is

$$Z = \sum_{\{i\}} e^{-\beta E_i}, \tag{15}$$

where $i$ denotes a microstate of the system, $E_i$ is the energy of the microstate, and $\sum_{\{i\}}$ is the summation over all microstates. To write the partition function for an ideal gas, we use Eq.(14) and Eq.(2) to make the following substitutions:

$$\sum_{\{i\}} \to \frac{1}{N!}\frac{1}{h^{3N}} \int d^3\mathbf{q}_1 \, d^3\mathbf{p}_1 \cdots \int d^3\mathbf{q}_N \, d^3\mathbf{p}_N \tag{16}$$

$$E_i \to \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m}. \tag{17}$$

From Eq.(15) the ideal gas partition function can then be written as

$$Z_{\text{ideal gas}} = \frac{1}{N!}\frac{1}{h^{3N}} \int_V d^3\mathbf{q}_1 \iint_{\text{all }\mathbf{p}} d^3\mathbf{p}_1 \cdots \int_V d^3\mathbf{q}_N \iint_{\text{all }\mathbf{p}} d^3\mathbf{p}_N \, \exp\left( -\beta \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} \right). \tag{18}$$

With Eq.(18) we have apparently achieved our goal. The partition function Eq.(18) defines the equilibrium thermodynamics for a system of $N$ non-interacting and identical particles confined to a volume $V$ at a temperature $T$. However, due to its gaussian nature, Eq.(18) can be further simplified. First, we note that the integrand does not have any dependence on the set of position coordinates $\{\mathbf{q}_k\}$. Therefore, we can evaluate the position integrals exactly to obtain

$$\int_V d^3\mathbf{q}_1 \iint_V d^3\mathbf{q}_2 \cdots \iint_V d^3\mathbf{q}_N = V^N. \tag{19}$$

Next, the integration over the momentum of each particle can be factored:

$$\int_{\text{all }\mathbf{p}} d^3\mathbf{p}_1 \iint_{\text{all }\mathbf{p}} d^3\mathbf{p}_2 \cdots \iint_{\text{all }\mathbf{p}} d^3\mathbf{p}_N \, \exp\left( -\beta \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} \right) = \prod_{k=1}^N \left( \iint_{\text{all }\mathbf{p}} d^3\mathbf{p}_k \, \exp\left( -\frac{\beta\mathbf{p}_k^2}{2m} \right) \right). \tag{20}$$

The momentum integrals in the product Eq.(20) only differ in their dummy variable of integration. Thus they are all identical. We can then write Eq.(18) as

$$Z_{\text{ideal gas}} = \frac{V^N}{N!}\frac{1}{h^{3N}} \left[ \iint_{\text{all }\mathbf{p}} d^3\mathbf{p} \, \exp\left( -\frac{\beta\mathbf{p}^2}{2m} \right) \right]^N. \tag{21}$$

To compute the momentum integral in Eq.(18), we write the $d^3\mathbf{p}$ integration element as $dp_x dp_y dp_z$. Since we are integrating over all of space we take the integrals along each coordinate direction from $-\infty$ to $+\infty$. We then have

$$
\iiint_{\text{all } \mathbf{p}} d^3\mathbf{p} \, \exp\left(-\frac{\beta\mathbf{p}^2}{2m}\right) = \int_{-\infty}^{\infty} dp_x \int_{-\infty}^{\infty} dp_y \int_{-\infty}^{\infty} dp_z \, e^{-\beta(p_x^2+p_y^2+p_z^2)/2m}
$$
$$
= \int_{-\infty}^{\infty} dp_x \int_{-\infty}^{\infty} dp_y \int_{-\infty}^{\infty} dp_z \, e^{-\beta p_x^2/2m} e^{-\beta p_y^2/2m} e^{-\beta p_z^2/2m}
$$
$$
= \left[\int_{-\infty}^{\infty} dp \, e^{-\beta p^2/2m}\right]^3 , \tag{22}
$$

where in the final line we used the fact that the integrations of $p_x$, $p_y$, and $p_z$ are identical in order to reduce the multiple integration to a product. To compute the momentum integral in Eq.(22), we use the identity $\int_{-\infty}^{\infty} dx \, e^{-ax^2} = \sqrt{\pi/a}$. We therefore find

$$
\int_{-\infty}^{\infty} dp \, e^{-\beta p^2/2m} = \sqrt{\frac{2\pi m}{\beta}} = \sqrt{2\pi m k_B T}. \tag{23}
$$

Returning to the partition function Eq.(21), we finally obtain

$$
Z_{\text{ideal gas}} = \frac{V^N}{N!} \frac{1}{h^{3N}} \left[(2\pi m k_B T)^{3/2}\right]^N = \frac{V^N}{N!} \left(\frac{2\pi m k_B T}{h^2}\right)^{3N/2} \tag{24}
$$

Eq.(24) is the most reduced form of the ideal gas partition function. To make the expression even cleaner, one often defines the quantity

$$
\lambda = \frac{h}{\sqrt{2\pi m k_B T}}, \tag{25}
$$

which has units of length and is called the **thermal de Broglie wavelength** of the particle. Since, by Eq.(25), higher temperatures are associated with shorter wave lengths, $\lambda$ can also be used as a proxy for the temperature of a system. With Eq.(25), the ideal gas partition function becomes

$$
\boxed{Z_{\text{ideal gas}} = \frac{1}{N!} \left(\frac{V}{\lambda^3}\right)^N , \quad \lambda = \frac{h}{\sqrt{2\pi m k_B T}}.} \tag{26}
$$

## 3   Physical Properties of an Ideal Gas

With the ideal gas partition function Eq.(26), we are now prepared to determine the basic physical properties of the gas. We are primarily interested in answering three questions

1. What is the probability distribution of speeds for the particles in the gas?

2. What is the average energy (as a function of temperature) of the ideal gas?

3. How does the pressure of a gas relate to temperature, volume, and number of particles of the gas?

   In these notes, we will answer the first question, and the final two questions will be left as homework assignments. The second can be answered by expressing Eq.(26) in terms of $\beta = 1/k_B T$ and recalling that the average energy of a system with partition function $Z$ is

$$
\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z. \tag{27}
$$

The final question requires that we introduce the concept of pressure into our system and that we show that the pressure $P$ is related to the free energy $F$ via

$$P = -\frac{\partial F}{\partial V}. \tag{28}$$

## 3.1 Speed distribution of particles in a gas

Our objective in this section is to determine the distribution of speeds for particles in a gas. First, let us recall what speed is. When a particle is moving in three-dimensions with velocity $\mathbf{v}$, the speed is defined as the magnitude of the particle's velocity. In terms of its components, the velocity could be written as $\mathbf{v} = (v_x, v_y, v_z)$. Thus, if we were to define $s$ as the speed of the particle, then we would have

$$s = \sqrt{v_x^2 + v_y^2 + v_z^2} \qquad \text{[Definition of speed of particle]}. \tag{29}$$

We want to find $p_{\text{speed}}(s)$ representing the probability distribution of speeds for the particle. Because $s$ can only be greater than or equal to $0$, this probability distribution must satisfy the normalization condition

$$1 = \int_0^\infty ds\, p_{\text{speed}}(s). \tag{30}$$

We begin our derivation of $p_{\text{speed}}(s)$ by recalling the Boltzmann distribution. Given a system in thermal equilibrium at temperature $T$, and given the energy $E_i$ of a microstate $i$, the probability that the system is in microstate $i$ is

$$p_i = \frac{e^{-\beta E_i}}{Z}, \tag{31}$$

where $Z$ is the partition function of the system. We will use Eq.(31) to compute the probability distribution for the velocities in the gas, and we will then use this result to find the probability distribution for speeds.

For our system, the partition function $Z$ is given by Eq.(18). It will first prove most useful to write it in terms of velocity variables rather than momentum variables. Noting that velocity is related to momentum via

$$\mathbf{p} = m\mathbf{v}, \tag{32}$$

we find

$$d^3\mathbf{p} = dp_x dp_y dp_z = (m\, dv_x)(m\, dv_y)(m\, dv_z) = m^3\, dv_x dv_y dv_z = m^3\, d^3\mathbf{v}. \tag{33}$$

Also, we can write the energy of all gas particles as

$$E = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} = \sum_{i=1}^N \frac{1}{2} m\mathbf{v}_i^2, \tag{34}$$

where we used the momentum-velocity relation $\mathbf{p} = m\mathbf{v}$ in the final equality. Therefore, Eq.(26) becomes

$$\begin{aligned}
Z_{\text{ideal gas}} &= \frac{m^{3N}}{N!} \frac{1}{h^{3N}} \int_V d^3\mathbf{q}_1 \int_{\text{all } \mathbf{v}} d^3\mathbf{v}_1 \cdots \int_V d^3\mathbf{q}_N \int_{\text{all } \mathbf{v}} d^3\mathbf{v}_N \exp\left(-\beta \sum_{i=1}^N \frac{1}{2} m\mathbf{v}_i^2\right), \\
&= \frac{V^N m^{3N}}{N!} \frac{1}{h^{3N}} \int_{\text{all } \mathbf{v}} d^3\mathbf{v}_1 \cdots \int_{\text{all } \mathbf{v}} d^3\mathbf{v}_N \exp\left(-\beta \sum_{i=1}^N \frac{1}{2} m\mathbf{v}_i^2\right)
\end{aligned} \tag{35}$$

where in the second line we evaluated all of the position integrals. To determine the probability distribution for the set of velocities $\mathbf{v}_1, \mathbf{v}_2, \ldots, \mathbf{v}_N$ of the the system, we can consider Eq.(35) and use it to seek out the

probability distribution $p_N(\mathbf{v}_1, \mathbf{v}_2, \cdots, \mathbf{v}_N)$ that satisfies the normalization condition

$$1 = \int_{\text{all } \mathbf{v}} d^3\mathbf{v}_1 \cdots \iint_{\text{all } \mathbf{v}} d^3\mathbf{v}_N \, p_N(\mathbf{v}_1, \mathbf{v}_2, \cdots, \mathbf{v}_N). \tag{36}$$

From Eq.(35), we find that we can define $p_N(\mathbf{v}_1, \mathbf{v}_2, \cdots, \mathbf{v}_N)$ as

$$\begin{aligned} p_N(\mathbf{v}_1, \mathbf{v}_2, \cdots, \mathbf{v}_N) &= \frac{1}{Z_{\text{ideal gas}}} \frac{V^N m^{3N}}{N!} \frac{1}{h^{3N}} \exp\left(-\beta \sum_{i=1}^{N} \frac{1}{2} m\mathbf{v}_i^2\right) \\ &= \frac{N!}{V^N} \left(\frac{h^2}{2\pi m k_B T}\right)^{3N/2} \frac{V^N m^{3N}}{N!} \frac{1}{h^{3N}} \exp\left(-\beta \sum_{i=1}^{N} \frac{1}{2} m\mathbf{v}_i^2\right) \\ &= \left(\frac{m}{2\pi k_B T}\right)^{3N/2} \exp\left(-\beta \sum_{i=1}^{N} \frac{1}{2} m\mathbf{v}_i^2\right) \end{aligned} \tag{37}$$

From the final form of the probability distribution in Eq.(37), we can infer that $p_N(\mathbf{v}_1, \mathbf{v}_2, \cdots, \mathbf{v}_N)$ can be expressed as the product

$$p_N(\mathbf{v}_1, \mathbf{v}_2, \cdots, \mathbf{v}_N) = p_1(\mathbf{v}_1) p(\mathbf{v}_2) \times \cdots \times p(\mathbf{v}_N), \tag{38}$$

where $p_1(\mathbf{v})$ is the single-particle velocity distribution defined as

$$p_1(\mathbf{v}) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-m\mathbf{v}^2/2k_B T}. \tag{39}$$

We wrote $\beta = 1/k_B T$ explicitly in the argument of the exponential because the temperature dependence is important in characterizing the final distribution.

Now, we are almost there in terms of finding an expression for the distribution of speeds of the particles in the gas. Eq.(38) tells us that all the particles have the same velocity distribution and therefore they must have the same speed distribution. We can use Eq.(39) to find the speed distribution by first writing the $\mathbf{v}$ in the expression in terms of its component form:

$$p_1(\mathbf{v}) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-m(v_x^2 + v_y^2 + v_z^2)/2k_B T}. \tag{40}$$

Now, the normalization condition for Eq.(40) is

$$1 = \int_{\text{all } \mathbf{v}} d^3\mathbf{v} \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-m\mathbf{v}^2/2k_B T} = \int_{-\infty}^{\infty} dv_x \int_{-\infty}^{\infty} dv_y \int_{-\infty}^{\infty} dv_z \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-m(v_x^2 + v_y^2 + v_z^2)/2k_B T}. \tag{41}$$

For a particle moving in three-dimensions, the speed is $s = (v_x^2 + v_y^2 + v_z^2)^{1/2}$, and although Eq.(41) expresses the probability distribution of velocities for each coordinate direction (i.e., for $v_x$, $v_y$, and $v_z$), it does not yet express the probability distribution of speed $s$. Instead, given the normalization condition in Eq.(30) and in Eq.(41), we are seeking a distribution $p_{\text{speed}}(s)$ such that

$$\int_0^{\infty} ds \, p_{\text{speed}}(s) = \int_{-\infty}^{\infty} dv_x \int_{-\infty}^{\infty} dv_y \int_{-\infty}^{\infty} dv_z \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-m(v_x^2 + v_y^2 + v_z^2)/2k_B T}, \tag{42}$$

where the speed is related to the components of velocity through $s = (v_x^2 + v_y^2 + v_z^2)^{1/2}$. Fortunately there is a straightforward way to make the transformation from $v_x$, $v_y$, and $v_z$ to the coordinates $(v_x^2 + v_y^2 + v_z^2)^{1/2}$. In a way similar to how we can move from $x$-$y$ coordinates to $r$ coordinates when we are performing a double
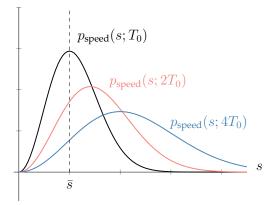
Figure 2: Plot of Maxwell-Boltzmann Distribution for various temperatures. Plot shows the probability distribution for speeds (Eq.(46)) of a molecule in an ideal gas for various temperatures. The point $\bar{s}$ marks the speed at which the distribution is maximized, and therefore represents the most likely speed. We see that as we increase temperature, the most likely speed increases as well.

integral over a function of $r = (x^2 + y^2)^{1/2}$, we can also move from $x$, $y$, and $z$ coordinates to $\rho$ coordinates when we are performing a triple integral over a function $\rho = (x^2 + y^2 + z^2)^{1/2}$. Namely, in two-dimensional polar coordinates, where $r = (x^2 + y^2)^{1/2}$, we have the identity

$$\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \, f\left(\sqrt{x^2 + y^2}\right) = \int_0^{\infty} dr \, 2\pi r \, f(r), \tag{43}$$

which we previously used to prove $\int_{-\infty}^{\infty} dx \, e^{-ax^2} = \sqrt{\pi/a}$. But in three dimensional spherical coordinates, where $\rho = \sqrt{x^2 + y^2 + z^2}$, we have the identity

$$\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \, f\left(\sqrt{x^2 + y^2 + z^2}\right) = \int_0^{\infty} d\rho \, 4\pi \rho^2 \, f(\rho). \tag{44}$$

Proving Eq.(44) (as does proving Eq.(43)) requires methods of multivariable calculus[2], but for this class we will take these statements to be true without proof. From Eq.(44), we can consider the right hand side of Eq.(42) and infer that the distribution of speeds $s$ is given by

$$\int_{-\infty}^{\infty} dv_x \int_{-\infty}^{\infty} dv_y \int_{-\infty}^{\infty} dv_z \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-m(v_x^2 + v_y^2 + v_z^2)/2k_B T} = \int_0^{\infty} ds \, 4\pi s^2 \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-ms^2/2k_B T}. \tag{45}$$

With Eq.(42) we can then claim that the distribution of speeds for a single particle is

$$\boxed{p_{\text{speed}}(s) = 4\pi s^2 \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-ms^2/2k_B T}.} \tag{46}$$

Eq.(46) is called the **Maxwell-Boltzmann distribution** of particle speeds. We can use it to compute the probability that the speed of one of our gas particles is within a certain range of speeds. A plot of Eq.(46) is shown in Fig. 2.

We note that there is a low probability of finding the particles with either speeds close to zero or speeds far from where the distribution is peaked. Using Eq.(46), we can find the value at which the distribution is

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[2]There is also an informal argument based on the fact that circular area increases by $dA = 2\pi r \, dr$ for changing 2D radius $r$, and spherical volume increases by $dV = 4\pi \rho^2 \, d\rho$ for changing 3D radius $\rho$.

peaked. Computing the speed $s = \bar{s}$ at which $dp_{\text{speed}}(s)/ds = 0$, we have

$$
0 = \frac{d}{ds} p_{\text{speed}}(s) \bigg|_{s=\bar{s}} = 4\pi \left( \frac{m}{2\pi k_B T} \right)^{3/2} \left[ 2\bar{s} - \frac{m\bar{s}^3}{k_B T} \right] e^{-m\bar{s}^2/2k_B T}, \tag{47}
$$

which, upon dropping the extraneous solution $\bar{s} = 0$, gives us

$$
\bar{s} = \left( \frac{2k_B T}{m} \right)^{1/2} \qquad \text{[Most likely speed of gas particles].} \tag{48}
$$

Eq.(48) is the *most likely* speed for a gaseous particle of mass $m$ in a system at a temperature $T$. We can use Eq.(48) to find the most likely speed for the various particles that make up the air at room temperature. Air is mostly composed of nitrogen gas $N_2$ and oxygen gas $O_2$. The masses of the nitrogen and oxygen molecules are

$$
m_{N_2} = 4.652 \times 10^{-26} \text{ kg}, \qquad m_{O_2} = 5.314 \times 10^{-26} \text{ kg}. \tag{49}
$$

Therefore, at room temperature (i.e $T = 298.3$ K), the most likely speed for the nitrogen and oxygen gas molecules in air is

$$
\bar{s}_{N_2} = 420.8 \text{ m/s}, \qquad \bar{s}_{O_2} = 393.7 \text{ m/s}. \tag{50}
$$

As a point of reference, if you're traveling 70 mph on the highway, then you're moving at 31.29 m/s. The speed of sound (also known as mach 1) is 340.27 m/s.

Another possibly relevant scale for the speed is the *average speed of a particle*. By the definition of average for a continuous distribution (and taking into account the possible speeds for the distribution), we can show

$$
\langle s \rangle = \frac{2}{\sqrt{\pi}} \left( \frac{2k_B T}{m} \right)^{1/2}, \tag{51}
$$

which is greater than Eq.(48). It makes sense that $\langle s \rangle > \bar{s}$ since, from Fig. 2, most of the probability distribution for speed lies to the right of $\bar{s}$.

Resource: Introduction to Statistical Physics
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