3

Thermodynamics

3.1 Preface

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3.2 Ideal gas

3.2.1 Theory

There are several commonly used models for the behaviour of gasses. A very simple yet powerful one is the **ideal gas** model: it describes gas particles as being perfect spheres which move around in an enclosed container and undergo elastic collisions with other particles and the walls of the container. In common conditions such as atmospheric pressure and temperatures around 300 [K], gasses such as helium (He), argon (Ar), nitrogen (N_2), oxygen (O_2) and carbon dioxide (CO_2) behave like ideal gasses (assuming no chemical reations take place). However, the ideal gas model fails under high pressures, low temperatures, chemical interactions and some physical processes such as adsorption or multipolar interactions.

The principle equation describing an ideal gas is the **ideal gas law**:

$$PV = nRT, \tag{3.1}$$

where (SI units in parentheses):

- P is the pressure of the gas (Pa),
- V is the volume of the container (m^3),
- n is the amount of gas (mol),
- R is the **gas constant**, $R = 8.314 \left[\mathrm{J\,K^{-1}\,mol^{-1}}\right]$, and

- T is the temperature of the gas (K).

Maxwell-Boltzman distribution

Mean free path

Temperature from energy

3.2.2 *Simulating an ideal gas using perfectly elastic spheres*

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Sphere-wall collision

An elastic collision between a particle and a wall causes the particle's velocity to flip in the direction of the wall's normal (Figure 3.1).

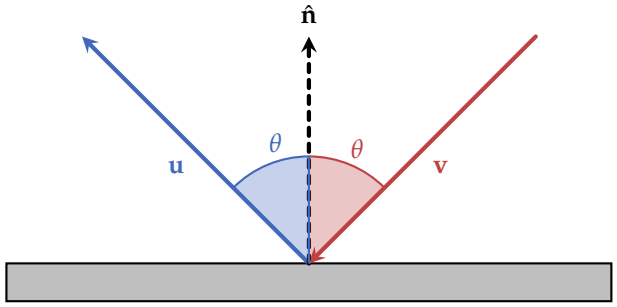

Figure 3.1: Collision of a particle and a wall. The particle bounces in such a way that the component of its velocity $\mathbf{v}$ in the direction of the wall's normal $\hat{\mathbf{n}}$ is flipped. The resulting velocity $\mathbf{u}$ has the same angle to $\hat{\mathbf{n}}$ as $\mathbf{v}$ does.

The component of $\mathbf{v}$ in the direction of $\hat{\mathbf{n}}$ is

$$\mathbf{v}_{\parallel} = \langle \mathbf{v}, \hat{\mathbf{n}} \rangle \hat{\mathbf{n}}. \tag{3.2}$$

Therefore, the component of $\mathbf{v}$ orthogonal to $\hat{\mathbf{n}}$ is

$$\mathbf{v}_{\perp} = \mathbf{v} - \mathbf{v}_{\parallel} = \mathbf{v} - \langle \mathbf{v}, \hat{\mathbf{n}} \rangle \hat{\mathbf{n}}. \tag{3.3}$$

In the case of $\mathbf{u}$, the orthogonal component is the same as that of $\mathbf{v}$, but the parallel component is inverted:

$$\begin{aligned} \mathbf{u}_{\perp} &= \mathbf{v}_{\perp}, \\ \mathbf{u}_{\parallel} &= -\mathbf{v}_{\parallel}. \end{aligned} \tag{3.4}$$

and altogether we get

$$\begin{aligned} \mathbf{u} &= \mathbf{u}_{\perp} + \mathbf{u}_{\parallel} \\ &= \mathbf{v} - \langle \mathbf{v}, \hat{\mathbf{n}} \rangle \hat{\mathbf{n}} - \langle \mathbf{v}, \hat{\mathbf{n}} \rangle \hat{\mathbf{n}} \\ &= \mathbf{v} - 2\langle \mathbf{v}, \hat{\mathbf{n}} \rangle \hat{\mathbf{n}}. \end{aligned} \tag{3.5}$$

Example 3.1 A simple sanity check

To make a simple validation of this equation, let's examine the case for a collision with a wall which is oriented in the xy-plane (i.e. its normal points in the z-direction): given the

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velocity $\mathbf{v} = \begin{bmatrix} v_x \\ v_y \\ v_z \end{bmatrix}$, Equation 3.5 becomes

$$\begin{aligned}
\mathbf{u} &= \mathbf{v} - 2\langle \mathbf{v}, \hat{\mathbf{n}} \rangle \hat{\mathbf{n}} \\
&= \begin{bmatrix} v_x \\ v_y \\ v_z \end{bmatrix} - 2\left\langle \begin{bmatrix} v_x \\ v_y \\ v_z \end{bmatrix}, \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix} \right\rangle \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix} \\
&= \begin{bmatrix} v_x \\ v_y \\ v_z \end{bmatrix} - 2(\cancel{v_x \cdot 0} + \cancel{v_y \cdot 0} + v_z \cdot 1) \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix} \\
&= \begin{bmatrix} v_x \\ v_y \\ v_z \end{bmatrix} - 2v_z \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix} \\
&= \begin{bmatrix} v_x \\ v_y \\ v_z \end{bmatrix} - 2 \begin{bmatrix} 0 \\ 0 \\ v_z \end{bmatrix} \\
&= \begin{bmatrix} v_x \\ v_y \\ v_z \end{bmatrix} + \begin{bmatrix} 0 \\ 0 \\ -2v_z \end{bmatrix} \\
&= \begin{bmatrix} v_x \\ v_y \\ -v_z \end{bmatrix},
\end{aligned}$$

as expected.

Note 3.1 Studying advice

The reader is encouraged to repeat the above calculation for the cases of walls oriented in the xz- and yz-planes.

When a sphere collides with a wall, the distance d from the center of the sphere to the wall is exactly r, the radius of the sphere. The distance between a point $\boldsymbol{P}$ and a plane $\boldsymbol{\pi}$ can be defined as follows: start from $\boldsymbol{P}$ and move along the direction $\pm\hat{\mathbf{n}}$ (where $\hat{\mathbf{n}}$ is the normal to the plane) until the plane is intersected at a point $\boldsymbol{B}$. The distance between $\boldsymbol{P}$ and $\boldsymbol{\pi}$ is then the length $\boldsymbol{PB}$ (Figure 3.2).

If we know a point $\boldsymbol{A}$ on the plane, then we can the vector $\mathbf{c}$ as starting at $\boldsymbol{A}$ and ending at $\boldsymbol{P}$ (i.e. corresponding to the line segment $\overline{\boldsymbol{AP}}$). The projection of $\mathbf{c}$ onto $\hat{\mathbf{n}}$ then gives the length $\boldsymbol{PM}$ (Figure 3.3).

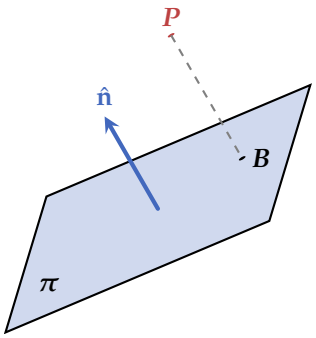

Figure 3.2: The distance between a point P and a plane π. The distance from P to the plane π is the length PB.

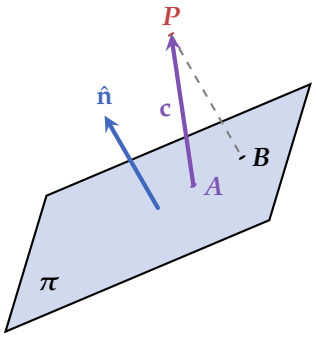

Figure 3.3: The vector $\mathbf{c}$ connects a known point on the plane A and the point P. Its projection on $\hat{\mathbf{n}}$ gives the distance PB.

Since $\hat{\mathbf{n}}$ is a unit vector, the projection of $\mathbf{c}$ onto it is simply the dot product between the two vectors, i.e. the distance d of point P and the plane π is

$$d = \langle \mathbf{c}, \hat{\mathbf{n}} \rangle. \tag{3.6}$$

Example 3.2 Distance of a point and a plane - sanity check

Let $P = (2, -4, 3)$. Let's calculate its distance to the three principle planes xy, xz and yz. We will use the origin as the point A, since all of these planes contain it. In each case, $\mathbf{c}$ will have as components the respective coordinates of P.

1. The normal to the xy-plane is $\hat{\mathbf{z}} = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}$. The dot product $\langle \mathbf{c}, \hat{\mathbf{n}} \rangle$ is therefore $d = \cancel{2 \cdot 0} + \cancel{(-4) \cdot 0} + 3 \cdot 1 = 3$.
2. The normal to the xz-plane is $\hat{\mathbf{y}} = \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix}$. The dot product $\langle \mathbf{c}, \hat{\mathbf{n}} \rangle$ is therefore $d = \cancel{2 \cdot 0} + (-4) \cdot 1 + \cancel{3 \cdot 0} = -4$.
3. The normal to the yz-plane is $\hat{\mathbf{x}} = \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}$. The dot product $\langle \mathbf{c}, \hat{\mathbf{n}} \rangle$ is therefore $d = 2 \cdot 1 + \cancel{(-4) \cdot 0} + \cancel{3 \cdot 0} = 2$.

As expected, the distance we get from P to each of the principle planes in $\mathbb{R}^3$ using Equation 3.6 is exactly the respective coordinate of P.

Sphere-sphere collision

Consider two solid spheres which have a single point of contact A. Let $m_1, r_1, \mathbf{x}_1$ and $\mathbf{v}_1$ be the mass, radius, position and velocity of the first sphere, and $m_2, r_2, \mathbf{x}_2$ and $\mathbf{v}_2$ the respective quantities for the second sphere (Figure 3.4). The line connecting the centers of the two spheres is in the direction $\hat{\mathbf{n}}$ (without loss of generality let us assume that the normal vector $\hat{\mathbf{n}}$ points from $\mathbf{x}_1$ towards $\mathbf{x}_2$). The unit vector $\hat{\mathbf{t}}$ is orthogonal to $\hat{\mathbf{n}}$ (and without loss of generality we will assume that it is oriented counter-clockwise from $\hat{\mathbf{n}}$).

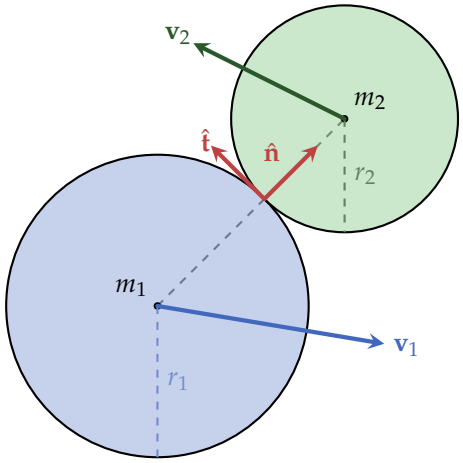

Figure 3.4: Text text text

Note that we did not define a coordinate system, nor the number of dimensions d for the problem. The only restriction is that $d \geq 2$.

Conservation of momentum means that the velocities of the spheres following the collision, $\mathbf{u}_1, \mathbf{u}_2$, are related to their velocities before the collision by

$$\begin{aligned} & m_1\mathbf{v}_1 + m_2\mathbf{v}_2 = m_1\mathbf{u}_1 + m_2\mathbf{u}_2 \\ \Rightarrow \quad & m_1\left(\mathbf{v}_1 - \mathbf{u}_1\right) = m_2\left(\mathbf{u}_2 - \mathbf{v}_2\right). \end{aligned} \tag{3.7}$$

Conservation of energy means that the velocities are also related by

$$\begin{aligned} & \frac{1}{2}m_1\|\mathbf{v}_1\|^2 + \frac{1}{2}m_2\|\mathbf{v}_2\|^2 = \frac{1}{2}m_1\|\mathbf{u}_1\|^2 + \frac{1}{2}m_2\|\mathbf{u}_2\|^2 \\ \Rightarrow \quad & m_1\left(\|\mathbf{v}_1\|^2 - \|\mathbf{u}_1\|^2\right) = m_2\left(\|\mathbf{u}_2\|^2 - \|\mathbf{v}_2\|^2\right). \end{aligned} \tag{3.8}$$

However, the forces involved in the collision can not have a component in the $\hat{\mathbf{t}}$ direction, and are limited to only point in the $\hat{\mathbf{n}}$ direction. Therefore, we can reduce the problem to this direction only by projecting all velocities involved in the problem on $\hat{\mathbf{n}}$, i.e. Equation 3.7 becomes

$$m_1\langle\mathbf{v}_1, \hat{\mathbf{n}}\rangle + m_2\langle\mathbf{v}_2, \hat{\mathbf{n}}\rangle = m_1\langle\mathbf{u}_1, \hat{\mathbf{n}}\rangle + m_2\langle\mathbf{u}_2, \hat{\mathbf{n}}\rangle. \tag{3.9}$$

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$$\begin{aligned}\mathbf{u}_1 &= \mathbf{v}_1 - \frac{2m_2}{m_1+m_2}\langle \mathbf{v}_1 - \mathbf{v}_2, \hat{\mathbf{n}}\rangle \hat{\mathbf{n}}, \\ \mathbf{u}_2 &= \mathbf{v}_2 + \frac{2m_1}{m_1+m_2}\langle \mathbf{v}_1 - \mathbf{v}_2, \hat{\mathbf{n}}\rangle \hat{\mathbf{n}}.\end{aligned} \tag{3.10}$$

To avoid reduntant calculations, we can factor out the common quantity of both velocities:

$$K = \frac{2}{m_1+m_2}\langle \mathbf{v}_1 - \mathbf{v}_2, \hat{\mathbf{n}}\rangle \hat{\mathbf{n}}, \tag{3.11}$$

yielding

$$\begin{aligned}\mathbf{u}_1 &= \mathbf{v}_1 - Km_2, \\ \mathbf{u}_2 &= \mathbf{v}_2 + Km_1.\end{aligned} \tag{3.12}$$

Reducing collision test complexity

Much like in the case of gravitational simulations, the number of calculations needed to resolve collisions between N particles is $N(N-1) = N^2 - N$, which grows like $\mathcal{O}\left(N^2\right)$. And also like in that case, we would like to reduce this complexity. One possible method is using a quad- or oct-tree as in the Barnes-Hutt algorithm mentioned in (REF!), but in the case of perfectly spherical particles which only experience instantaneous elastic collisions, there are much simpler method.

The first and simplest of these methods is the **Axis-Aligned Bounding Box**, or simply **AABB**. In the 2-dimensional case, a **bounding box** (BB) of an object is the minimal rectangular area surrounding it completely (i.e. that contains the entire object within it). An AABB of an object is (as the name suggests) a BB with sides parallel to the 2 axes (Figure 3.5).

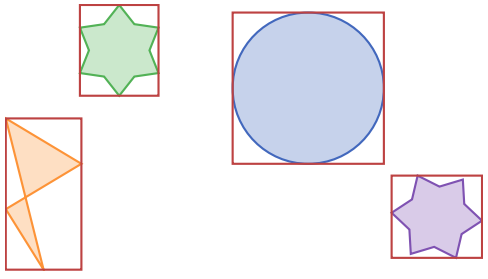

Figure 3.5: Axis-Aligned Bounding Boxes (AABBs) for different objects in 2-dimensions.

In the case of a circle of radius r, its AABB is a square of side $2r$ with the sides parallel to the x and y axes, respectively, and sharing its center with the circle. Therefore, given a circle of radius r centered at (x, y), its AABB is the square with the two opposing corners

$$\begin{aligned}\mathbf{c}_{\text{LL}} &= (x - r, y - r), \\ \mathbf{c}_{\text{UR}} &= (x + r, y + r),\end{aligned} \tag{3.13}$$

where LL stands for "Lower-Left" and UR stands for "Upper-Right".

When two objects collide, their AABBs necessarily overlap (Figure 3.6). This means that if we know that two circles have no overlap in their AABBs, we can skip the check whether they collide or not, as it is entirely redundant. Luckily, checking overlaps in AABBs can be very fast compared to checking even the simplest collision, and this way we gain advantage in computation speed. Let's see how it is done.

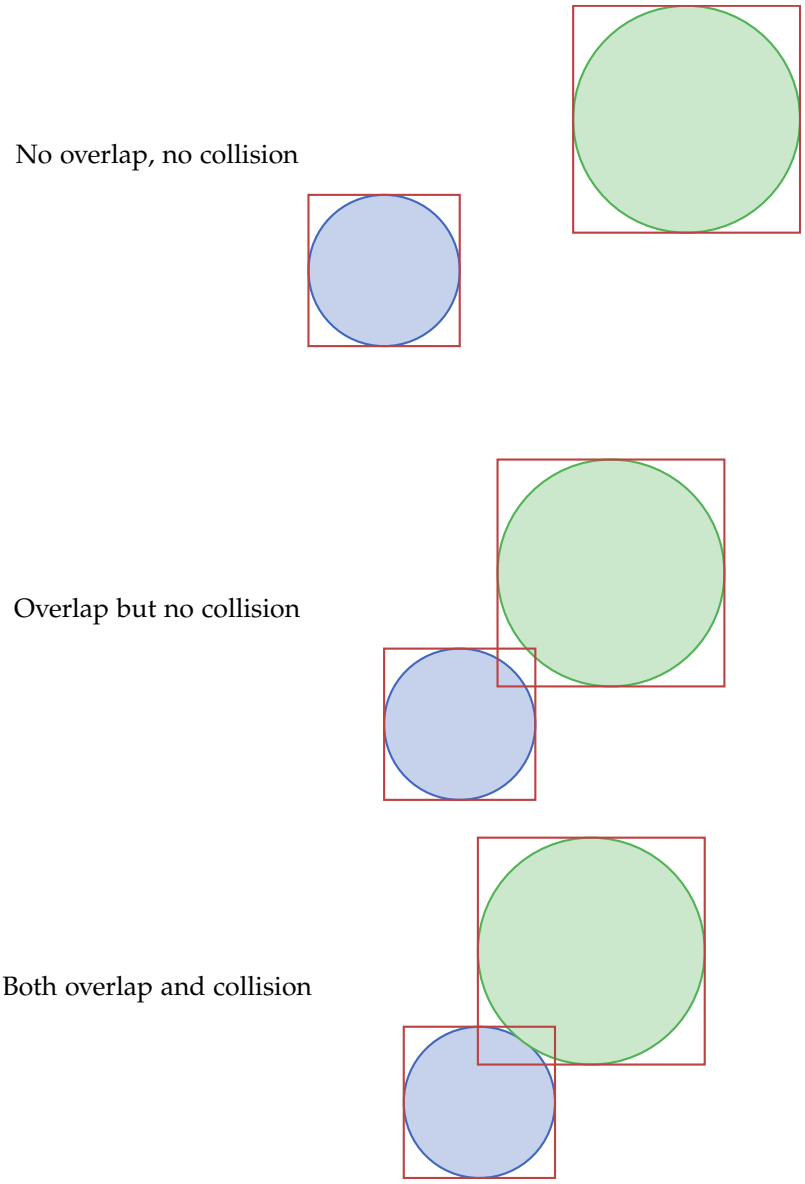

Figure 3.6: AABBs of twho circles. There can be three different relations between the circles in regards to their AABBS - no overlap between the AABBs and no collision between the circles (top), and overlap of the AABBs but no collision (middle), and an overlap with a collision (bottom). A collision between the circles necessarily means that there is also an overlap between the AABBs.

We first examine the conditions for an overlap in a single dimension: given two intervals $I_1 = [a, b]$ and $I_2 = [c, d]$, let's assume without loss of generality that a is the smallest number of the four quantities a, b, c and d. The condition for overlap between the two intervals is simply $c < b$, i.e. that the left-most point of I_2 is to the *left* of the right-most point of I_1 (Figure 3.7).

We can consider an AABB across each axis to be an interval: if the lower-left and upper-right corners of the AABB are at $\mathbf{c}_{\mathrm{LL}} = (x_1, y_1)$

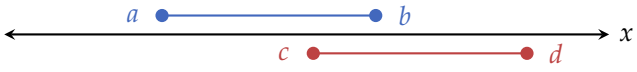

Figure 3.7: For two intervals $(a, b), (c, d)$ (assuming $a < b, c, d$) to overlap, the condition $c < b$ must be fulfilled.

and $\mathbf{c}_{\text{UR}} = (x_2, y_2)$, respectively, then the vertical sides of the AABB are represented as an interval $I_{\text{horiz}} = [x_1, x_2]$, and the horizontal sides by $I_{\text{vert}} = [y_1, y_2]$ (Figure 3.8).

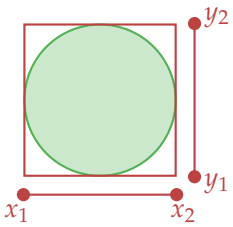

Figure 3.8: The sides of an AABB as two intervals $I_{\text{horiz}} = [x_1, x_2]$ and $I_{\text{vert}} = [y_1, y_2]$.

Two AABBs overlap **if and only if** both their horizontal and vertical intervals overlap (Figure 3.9)

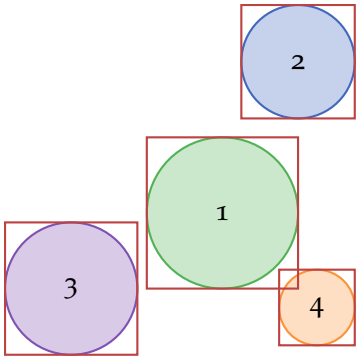

Figure 3.9: Four circles with different overlaps between their AABBs: 1-2 and 2-4 overlap horizontally only. 1-3 and 3-4 overlap vertically only. 1-4 overlap in both directions.

3.3 *Brownian dynamics*