# Dilute Gases and DSMC

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## 1   Introduction

A system may be characterized as dilute based on the "average" spacing between its molecules

$$\delta \sim \sqrt[3]{\frac{1}{n}} \quad \text{or} \quad \frac{\delta}{\sigma} \sim \sqrt[3]{\frac{1}{n\sigma^3}}$$

where $n$ is the number density (number of atoms per unit volume) and $\sigma$ is the effective "diameter" of the molecule (referring to, for example, a Lennard-Jones model). We see that the relevant quantity here is the non-dimensional number density $n^* = n\sigma^3$. If $n^* \ll 1$ , then the system can be described as dilute, in other words, the volume per particle $(\sim n^{-1})$ is much larger than the volume of the particle $(\sim \sigma^3)$, or alternatively, the relative spacing $\delta/\sigma$ is large.

Consider a simple (monoatomic gas) at atmospheric pressure with

$$\rho \sim 1\frac{\text{Kg}}{\text{m}^3}, \quad \sigma \approx 3.6 \times 10^{-10}\text{m}$$

The number density $n$ is given by

$$n = \frac{\rho}{M}\frac{\text{Kmoles}}{\text{m}^3} = \frac{\rho \times 6.023 \times 10^{26}}{M}\frac{\text{molecules}}{\text{m}^3}$$

where $M$ =molecular weight. Plugging in,

$$M \sim 30\frac{\text{Kg}}{\text{Kmole}} \Rightarrow n \simeq 2 \times 10^{25}\frac{\text{molecules}}{\text{m}^3} \text{ or } n^* \approx 0.001$$

As we can see from the example studied here, simple gases at atmospheric conditions meet the dilute gas criterion. Air, although made from diatomic gases, can for a number of applications, be thought of as a simple, dilute gas.

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In a dilute system one expects collisions between particles to be infrequent and, because of the absence of other interactions, particles to travel most of the time in straight lines. We will show below that in a dilute system the average distance traveled by molecules between successive collisions with other molecules, known as the mean free path $\lambda$, is given by

$$\lambda = 1/\left(\sqrt{2}\pi n \sigma^2\right)$$

For the particular gas we are studying here we get $\lambda \approx 5 \times 10^{-8} m$. This number is significantly larger than $\sigma$ and thus we see that our assumption that particles travel in straight lines most of the time seems to be justified. To generalize the above result to all dilute gases, we write

$$\frac{\lambda}{\sigma} = \frac{1}{\sqrt{2}\pi n \sigma^3}$$

Thus, $\lambda \gg \sigma$ if $n^* \ll 1$.

From this simple analysis and the observation that in the absence of electrostatic interactions the force-field between molecules decays to negligible levels within $3-4\sigma$, we conclude:

1. Molecules in a gas to a good approximation most of the time do not feel forces from other molecules ($\delta \gg \sigma$). As a result, they travel in straight lines until they have an "encounter" with another molecule.

2. Since $\lambda \gg \sigma$, the time taken by the encounter (more generally the time that the molecules are in the force-field of each other) is negligible, compared to the motion timescale (time between collisions).

3. A condition for all of the above to be true is $n\sigma^3 \ll 1$, that is, the average volume available to a particle is much larger than the volume of a particle.

The above conclusions support the use of a "billiard-ball" or hard-sphere model in which particles of diameter $d \approx \sigma$ only interact during hard-sphere collisions.

Note that in liquids $\rho_\ell \sim 10^3 \rho_g \Rightarrow n\sigma^3 \sim 0(1)$ i.e. $\delta \sim \sigma$

## 2    The Hard Sphere Gas in Equilibrium

The hard sphere gas is a very useful and powerful model. We can analyze very complex phenomena in gases by using this model which is a good approximation of physical reality.

We will first find the probability distribution of molecular velocities in equilibrium. We will use the general statistical mechanical result that for a system in equilibrium

at temperature $T$, the probability, $P(S)$, of a particular state $S$ of the system is proportional to

$$P(S) \propto \exp\{-E(S)/(kT)\}$$

where $E(S)$ is the energy of the system in state $S$ and $k = 1.38 \times 10^{-23} J/K$ is Boltzmann's constant. For our $N$-molecule billiard-ball model,

$$E = \sum_{i=1}^{N} \frac{1}{2} m U_i^2$$

where

$$U^2 = |\vec{U}|^2 = U_x^2 + U_y^2 + U_z^2.$$

We immediately see that the lack of interaction between molecules manifests itself in the independence of the probability distribution functions of the $N$ molecules i.e.

$$
\begin{aligned}
P\left(\vec{U}_1, \vec{U}_2, \ldots, \vec{U}_N\right) &= C \exp\left\{-\frac{m\left(U_1^2 + U_2^2 + U_3^2 + \ldots + U_N^2\right)}{2kT}\right\} = \\
&= P\left(\vec{U}_1\right) \cdot P\left(\vec{U}_2\right) \cdot P\left(\vec{U}_3\right) \ldots P\left(\vec{U}_N\right)
\end{aligned}
$$

where $C$ is a normalization constant.

This property allows us to define and use the single-molecule distribution function

$$f\left(\vec{U}\right) = A\, e^{-\frac{mU^2}{2kT}}$$

where

$$A = \left(\frac{m}{2\pi kT}\right)^{3/2}$$

is the appropriate normalization such that

$$\int_{All\,\vec{U}} f(\vec{U})\, d\vec{U} = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f(\vec{U})\, dU_x\, dU_y\, dU_z = 1.$$

This is the famous Maxwell-Boltzmann distribution of velocities (in equilibrium). Note that since the distribution is isotropic the angular parts can be integrated to obtain the probability distribution of molecular *speeds* ($U = |\vec{U}|$) which is given by

$$\hat{f}(U)dU = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} U^2\, e^{-\frac{mU^2}{2kT}}\, dU.$$

## 2.1 Pressure in a dilute gas

As a simple example of the usefulness of $f$, consider the pressure in a dilute gas. The pressure is the force per unit area exerted on a surface (real or imaginary) in contact with the gas. Let us assume, without loss of generality, that the normal to the surface coincides with the $x$-direction. We will consider particles striking the surface moving from left to right ($U_x > 0$). The number of such particles of velocity $U_x$ that will collide with this surface in time $\Delta t$, is equal to the number of particles in a volume $AU_x\Delta t$ where $A$ is the area of the surface. Since the particles are uniformly distributed in space, this number can be written as $nfAU_x\Delta t$. To find the total momentum exchange per unit time we need to consider the change of momentum ($-2mU_x$) upon impact and integrate over all velocity classes i.e.,

$$\frac{1}{\Delta t} \int_0^\infty \int_{-\infty}^\infty \int_{-\infty}^\infty -2mU_xU_xnfA\Delta t dU_x\, dU_y\, dU_z$$

where the integration in $U_x$ goes from 0 to $\infty$ because we are only integrating over particles traveling from left to right ($U_x > 0$). The pressure is given by the negative of this quantity (force by particles on wall is equal and opposite to force of wall on particles) divided by the surface area, i.e.

$$P = \frac{1}{A\Delta t} \int_0^\infty \int_{-\infty}^\infty \int_{-\infty}^\infty 2mU_xU_xnfA\Delta t dU_x\, dU_y\, dU_z = nkT$$

We have obtained the ideal gas law.

In the above calculation we have used the following: If

$$I_n = \int_0^\infty x^n e^{-\alpha x^2} dx$$

then

$$I_0 = \frac{1}{2}\left(\frac{\pi}{\alpha}\right)^{1/2}, \quad I_1 = \frac{1}{2\alpha}, \quad I_2 = \frac{1}{4}\left(\frac{\pi}{\alpha^3}\right)^{1/2}$$

Note that in the above discussion we assumed that the molecules are specularly reflected at the wall, that is, the velocity of the particle in the direction normal to the wall is simply reversed by the collision with the wall. This is possible because *in equilibrium* this model is equivalent to a diffuse reflection model where molecules are re-emitted from the surface with a new velocity drawn from the wall distribution. This is because, for the gas and the wall to be in equilibrium, to a good approximation, the wall distribution $f_w(\vec{U})$ is such that the gas perceives an infinite expanse of *the same gas* behind the wall, i.e. $f_w(\vec{U}) = f(\vec{U})$. Writing the pressure as the sum of the momenta imparted by the incoming and emitted particles,

$$
\begin{aligned}
P &= \int_0^\infty \int_{-\infty}^\infty \int_{-\infty}^\infty mU_xU_xnf dU_x\, dU_y\, dU_z + \int_{-\infty}^0 \int_{-\infty}^\infty \int_{-\infty}^\infty mU_x'U_x'nf_w' dU_x'\, dU_y'\, dU_z' \\
&= \int_0^\infty \int_{-\infty}^\infty \int_{-\infty}^\infty 2mU_xU_xnf dU_x\, dU_y\, dU_z = nkT
\end{aligned}
$$

# 3 Collision Frequency and Mean Free Path in equilibrium

Clearly one of the most important quantities in understanding the behavior of a gas is the mean free path and the collision frequency or its inverse, the time between collisions. To find these we will look at the motion of one "test" molecule in time $\Delta t$. Let us assume that all other particles are stationary, and that, although the moving test particle will be scattered by collisions, its trajectory is still linear. As the test molecule moves, it will experience a collision with any molecule in a tube of radius $d$. Then the number of collisions experienced is:

$$N_{coll} = n\pi d^2 \langle U \rangle \Delta t$$

where $\langle U \rangle$ is the test molecule velocity. This expression is obviously an approximation to the true number of collisions because the volume covered $(\pi d^2 \langle U \rangle \Delta t)$ neglects the "elbows" of the true trajectory of the particle. We can account for the fact that all other particles are moving by using the relative velocity between the test molecule and all other molecules by replacing $\langle U \rangle$ with the average relative velocity between two particles

$$\langle U_r \rangle = \int_{\text{All } \vec{U}_1} \int_{\text{All } \vec{U}_2} f\left(\vec{U}_1\right) f\left(\vec{U}_2\right) \left|\vec{U}_1 - \vec{U}_2\right| d\vec{U}_1 d\vec{U}_2$$

$$= \frac{4}{\sqrt{\pi}} \sqrt{\frac{kT}{m}}$$

so the number of collisions per unit time is given by

$$\frac{N_{coll}}{\Delta t} = n\pi d^2 \langle U_r \rangle$$

and the mean time between collisions is $\tau = 1/\left(n\pi d^2 \langle U_r \rangle\right)$. The number of collisions taking place per unit time per unit volume in the gas is

$$\Gamma = \frac{1}{2} n \frac{1}{\tau} \tag{1}$$

The average distance traveled between collisions, i.e., the mean free path, is then given by $\lambda = \langle U \rangle \tau$ where

$$\langle U \rangle = \int_{\text{All } \vec{U}} f\left(\vec{U}\right) |\vec{U}| d\vec{U} = \int_0^\infty \hat{f}\left(U\right) U dU = \sqrt{\frac{8kT}{\pi m}}$$

is the average particle speed, and therefore,

$$\lambda = \frac{1}{\sqrt{2}\pi n d^2}.$$

# 4 Molecular Simulation of Hard-Sphere Systems

The simulation of "hard" systems is different from the standard methods used in molecular dynamics. There are two main reasons for this. First, hard spheres spend most of their time traveling in straight lines so it is very inefficient (and pointless) to integrate straight-line trajectories

$$\left( m\frac{d^2\vec{r}}{dt^2} = 0 \right)$$

numerically. Second, when a collision occurs it is instantaneous and the force exerted between the spheres is impulsive. The best way to handle the diverging (instantaneously) force is to apply convervation principles relating particle velocities before and after the collision.

For these reasons the approach typically taken, known as hard-sphere molecular dynamics, can be summarized as follows. Let the position and velocity of particle $i$ at some time (initially) be $\vec{r}_i$ and $\vec{v}_i$ respectively.

1. Locate the next collsion in the system (found by solving $|\vec{r}_i - \vec{r}_j + (\vec{v}_i - \vec{v}_j)\delta t| = d$ for the shortest $\delta t$ for all pairs $(i, j)$ of molecules)

2. Move all particles forward (in straight lines) until this collision occurs

3. Process the collision for the colliding pair (calculate post-collision velocities)

4. Go to 1.

Although this method is significantly faster than "regular" molecular dynamics, it is not as efficient as the method discussed in the next section. Note that the above algorithm is an $O(N^2)$ algorithm, that is, by doubling the number of particles in the system the work that needs to be done quadrouples. This is because there are $\frac{1}{2}N^2$ possible collision pairs that need to be checked in step 1 above.

An order $N$ algorithm may be obtained by *only recomputing* future collision times (with all the molecules in the system) for the pair that has just collided. This provides substantial savings, but the method remains inefficient: The most significant disadvantange of the improved method comes from the fact that although each molecule on average will travel freely for time $\tau$ before it has a collision, collisions happen in the system continuously and the simulation proceeds at a much smaller timestep $\Delta t \ll \tau$. An efficient simulation method which addresses this disadvantage is described in the next section.

# 5 The Direct Simulation Monte Carlo

The Direct Simulation Monte Carlo is an efficient algorithm that uses the fact that although the time between subsequent collisions in the system is small, the time between collisions of the same molecule is $\tau$. The main idea behind DSMC is to decouple collisions and particle motion to achieve efficiency.

We expect that if we were to "discretize" particle motion in time (timestep $\Delta t$) and space (cell size $\Delta x$) these would need to be small compared to the characteristic timescales and lengthscales of the gas behavior, $\tau$ and $\lambda$ respectively. However, now $\Delta t$ can be such that $\Delta t < \tau$ rather than $\Delta t \ll \tau$ that we had in the hard-sphere molecular dynamics method.

The DSMC algorithm that follows this idea is given below:

1. Advance particles from $\{\vec{r}_i\}$ to $\{\vec{r}_i + \vec{U}_i \Delta t\}$ ignoring collisions. Here { } means "set of all."

2. Apply boundary conditions (wall, inlet/outlet...)

3. Sort particles in cells of size $\Delta x$

4. Apply collisions that should have taken place in time $\Delta t$ in each cell by randomly choosing collision partners from the given cell. This is given by $\Gamma_{ne} \Delta t \, V_{cell}$ where $V_{cell}$ is the volume of the cell and $\Gamma_{ne}$ is the *non-equilibrium* collision rate (per unit volume and time). [An implementation of the collision routine without explicitly calculating $\Gamma_{ne}$ can be found in the book by Bird given below.]

5. Repeat

The stochastic nature of the collision process (collision pairs are chosen randomly) makes this an $O(N)$ algorithm. Additionally particles in the system may be interpreted as computational particles, each representing a large number ($N_{effective}$) of real particles. This reduces the computational cost significantly.

This simple algorithm has beeen shown to capture gaseous hydrodynamics with great reliability and accuracy. For examples see Bird, "Molecular Gas Dynamics and the Direct Simulation of Gas Flows," (1994). Simple DSMC codes can be downloaded from http://www.algarcia.org/nummeth/Programs2E.html. A visual DSMC program can be downloaded from www.gab.com.au.

Of particular importance to the accuracy of this method is the use of small timestep $\Delta t$ and cell size $\Delta x$. The effect of the time step is obvious: the longer particles move without collsions the higher the probability of reaching places that they would normally not have reached because of the scattering effect of the collisions. The effect of the cell size is similar: since collision partners are chosen from the

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same cell, large cells allow collisions between particles that would have never collided because they are simply too far apart.