Introduction to Modeling and Simulation
Lecture 8: Dilute Gases

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1 Introduction

Consider a simple (monoatomic gas) at atmospheric pressure with density

$$\rho \sim 1 \frac{Kg}{m^3}$$

The number density n is given by

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

where M =molecular weight and n =number density with

$$M \sim 30 \frac{Kg}{Kmole} \Rightarrow n \simeq 2 \times 10^{25} \; \frac{molecules}{m^3}$$

The "average" spacing between molecules is

$$\delta \sim \sqrt[3]{\frac{1}{n}} = 3.6 \times 10^{-9} \; m \gg \sigma \left(\approx 4 \times 10^{-10} m \right)$$

where σ is the effective "diameter" of the molecule. (See, for example, a Lennard-Jones model).

We will show soon that the average distance traveled by molecules between successive collisions with other molecules known as the mean free path λ, is

$$\lambda = 1 / \left(\sqrt{2} \pi n \sigma^2 \right) \; \approx 5 \times 10^{-8} m.$$

In the above evaluation we took $\sigma \approx 4 \times 10^{-10} m$. From the above,

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

From this simple analysis and the observation that in the absence of electrostatic interactions the force field between molecules decays to negligible levels within $2-3\sigma$, we conclude:

1. Molecules in a gas to a good approximation do not feel forces from other molecules ($\delta \gg \sigma$). As a result, they travel in straight lines until they have a collision with another molecule.
2. Since $\lambda \gg \sigma$, the time taken by the collision (more generally the time that the molecules are in the force-field of each other) is negligible.

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

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 very good approximation of physical reality.

We will first find the probability distribution of molecular velocities. 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

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

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,

$$E = \sum_{i=1}^{N} \frac{1}{2} m \vec{U}_i^2$$

where

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

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.

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

where C is a normalization constant.

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

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

where

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

is the appropriate normalization such that

$$\int_{\text{All } \vec{U}} f(\vec{U}) d\vec{U} = 1.$$

This is the famous Maxwell-Boltzmann distribution for the distribution of velocities of a gas in equilibrium. Note that since the distribution is isotropic the angular parts can be integrated to obtain the probability distribution of particle speed $U = |\vec{U}|$

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

As a simple example of the usefulness of f, consider the pressure in a 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. The number of particles of velocity U_x that will collide with this surface in time Δt, 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, the latter is given by $nfAU_x\Delta t$. To find the total momentum exchange per unit time and unit area we need to consider the change of momentum ($2mU_x$) upon impact of all velocity classes i.e.,

$$P = \frac{1}{A\Delta t} \int_0^\infty \int_{-\infty}^\infty \int_{-\infty}^\infty 2mU_x U_x n f A \Delta t d\vec{U} = nkT$$

where the integration in U_x goes from 0 to ∞. We have obtained the ideal gas law.

3 Collision Frequency and Mean Free Path

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 Δt. 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 σ. Then the number of collisions experienced is:

$$N_{coll} = n\pi\sigma^2 \, U\Delta t,$$

where U is the test molecule velocity. This expression is obviously an approximation to the true number of collisions because the volume covered ($\pi\sigma^2 U\Delta t$) 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 U with the mean relative velocity between two particles

$$\begin{aligned} \langle U_r \rangle &= \int_{\mathrm{All}\ \vec{U}_1} \int_{\mathrm{All}\ \vec{U}_2} f\left(\vec{U}_1\right) f\left(\vec{U}_2\right) \left|\vec{U}_1 - \vec{U}_2\right| d\vec{U}_1 d\vec{U}_2 \\ &= \frac{4}{\sqrt{\pi}} \sqrt{\frac{kT}{m}} \end{aligned}$$

so the number of collisions per unit time is given by

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

and the time between collisions is $\tau = 1/\left(n\pi\sigma^2\langle U_r\rangle\right)$

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

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

is the average particle speed, and therefore,

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

4 The Direct Simulation Monte Carlo

An exact simulation of the hard-sphere system typically proceeds as follows: Given an initial condition, the intersection points of the trajectories of all $\frac{N^2}{2}$ pairs of molecules are calculated. The collision that happens at the earliest time is processed (post collision velocities for the colliding pair are calculated) and the process is repeated. However, this algorithm has an unfavorable scaling (N^2) and the total time simulated is limited by the small time interval between subsequent collisions, $\Delta\tau$.

We now have the tools to "design" a simulation algorithm that will capture the physics of gaseous behaviour in the non-equilibrium case that the distribution function is not known.

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 $\tau \gg \Delta\tau$. The main idea behind DSMC is to decouple collisions and particle motions to achieve efficiency.

We expect that if we were to "discretize" particle motion in time (timestep Δt) and space (cell size Δx) these would need to be small compared to the characteristic timescales and lengthscales of the gas behavior, τ and λ respectively.

The DSMC algorithm that follows this idea is given below:

1. Advance particles from $\{\vec{r}_i\}$ to $\left\{\vec{r}_i + \vec{U}_i \Delta t\right\}$ ignoring collisions
2. Apply boundary conditions (wall, inlet/outlet...)
3. Sort particles in cells of size Δx
4. Apply collisions that should have taken place in time Δt in each cell by randomly choosing collision partners from the given cell. This is given by $\Gamma \Delta t \ V_{cell}$ where V_{cell} is the volume of the cell and

   $$\Gamma = \frac{1}{2} n \frac{1}{\tau} = \frac{1}{2} n^2 \pi \sigma^2 \langle U_r \rangle$$

   is the collision rate per unit volume and time.
5. Repeat

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. Of particular importance to the accuracy of this method is the use of small timestep Δt and cell size Δx. The effect of the time step is obvious: the longer particles move without collsions the higher the probability of reaching places that they should 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 same cell, large cells allow collisions between particles that would have never collided because they are simply too far apart.