Stochastic Collision KMC (DSMC)

Consider a Hamiltonian system of particles that interact via a pairwise spherically-symmetric potential such as the Lenard-Jones potential

$$\mathcal{U}(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \sum_{i \neq j} \mathcal{U}(r_{ij} = \| \mathbf{r}_i - \mathbf{r}_j \|)$$

Consider the distribution functions:

(1) $f(\mathbf{r}, \mathbf{p}; t)$ = single-particle probability DF of finding a particle at $\mathbf{r}$ with momentum $\mathbf{p} = m\mathbf{v}$

(2) $f_2(\mathbf{r}_1, \mathbf{p}_1; \mathbf{r}_2, \mathbf{p}_2; t)$ two-particle PDF

The atomistically-defined distribution function for a particular configuration (initial configuration) is

$$f_z(r,p;t') = \sum_{j=1}^{N} \delta(r-r_j)\,\delta(p-p_j)$$

with initial condition $(r(t), p(t)) = z$

Then

$$f(r,p;t) = \langle f_z(r,p;t) \rangle_z$$

is just an average over all initial conditions (ensemble average)

From the equations of motion we get:

$$\frac{\partial}{\partial t} f_t(r,p;t) = -\sum_{j=1}^{N} \left(\frac{\partial r_j}{\partial t} \cdot \frac{\partial}{\partial r} + \frac{\partial p_j}{\partial t} \cdot \frac{\partial}{\partial p} \right) \times \delta(r - r_j(t))\ \delta(p - p_j(t))$$

$$= -\sum_{j=1}^{N} \left[\frac{p_j}{m} \cdot \frac{\partial}{\partial r} + F_e(r_j) \cdot \frac{\partial}{\partial p} \right] \delta(r - r_j(t))\,\delta(p - p_j(t))$$

F_e: external force

$$F = -\partial U / \partial r$$

$$+ \sum_{k \neq j} F(r_{kj}) \cdot \frac{\partial}{\partial p}\ \delta(r - r_j(t))\,\delta(p - p_j(t))$$

and now average over initial conditions

$$\frac{\partial}{\partial t} f(r,p;t) = \left(-\frac{p}{m}\cdot\frac{\partial}{\partial r} + F_e\cdot\frac{\partial}{\partial p}\right) f$$

$$+\left[\frac{\partial f}{\partial t}\right]_{pairs}$$

↑ Liouville operator for a single particle in an external field

Here

$$\left[\frac{\partial f}{\partial t}\right]_{pairs} = \int F(\|r-r'\|)\cdot\frac{\partial}{\partial p} f_2 \cdot dr'\,dp'$$

requires the two-particle PDF $f_2(r,p;r',p';t)$. In general an infinite hierarchy of BBGKY equations { Bogolyubov, Born-Green, Kirkwood, Yvon

For a low-density gas, or as an approximation for hydrodynamics of liquids, we can represent the two-particle term as an integral over collisions of particles that are nearby. This involves some approximations:

(1) Particle interactions are very localized in space and time (instantaneous collisions): Markov Chain model

(2) Molecular chaos:

$$f_2(r,p,r',p') \approx f(r,p)\, f(r',p')$$

By approximating

$$\left[\frac{\partial f}{\partial t}\right]_{pairs} \approx \left[\frac{\partial f}{\partial t}\right]_{collisions} =$$

$$= \int dp' dp_1' dp_2' \Big[w(p, p' \mid p_1, p_2') f(r, p_1) f(r, p_2)$$

transition probability

$p_1 + p_2 \rightarrow p + p'$

distributions

$$- w(p_1, p_2 \mid p, p') f(r, p) f(r, p') \Big]$$

$p + p' \rightarrow p_1 + p_2$

Which is a Master equation: Boltzmann equation

The transition probabilities must satisfy certain physical principles, but are otherwise arbitrary and a modeling (coarse-graining) choice:

(1) Momentum must be conserved

$$p_1 + p_2 = p + p'$$

(2) Energy must be conserved. For equal masses

$$p_1^2 + p_2^2 = p^2 + (p')^2$$

(3) Detailed balance: Time-reversal and particle exchange symmetries

$$\begin{cases} W(p,p' \mid p_1,p_2) = W(p_1,p_2 \mid p,p') \\ w(p',p \mid p_2,p_1) = W(p,p' \mid p_1,p_2) \end{cases}$$

Detailed balance ensures stationarity of the Gibbs-Boltzmann momentum distribution, known as the Maxwell-Boltzmann distribution:

$$f_{eq}(r,p) = \frac{\bar{\rho}(r)/m}{\left[2\pi m k \bar{T}(r)\right]^{3/2}} \cdot e^{-\frac{(p-\bar{p}(r))^2}{2mk\bar{T}(r)}}$$

where the local mean density $\bar{\rho}(r)$, velocity $\bar{v}(r) = \bar{p}(r)/m$, and temperature $\bar{T}(r)$, appear

To see this, rewrite the collision integral using time reversal symmetry

$$\left[\frac{\partial f}{\partial t}\right]_{coll} = \int dp' dp_1' dp_2' \cdot W(p,p'|p_1|p_2)$$

must vanish at equilibrium $\longrightarrow \left[f(r,p_1) f(r,p_2) - f(r,p) f(r,p') \right]$

$$e^{\alpha(p_1-\bar{p})^2} e^{\alpha(p_2-\bar{p})^2} \stackrel{?}{=} e^{\alpha(p-\bar{p})^2} e^{\alpha(p'-\bar{p})^2}$$

$$e^{\alpha\left[(p_1^2+p_2^2)-2(p_1+p_2)\cdot\bar{p}\right]} = e^{\alpha\left[(p^2+p'^2)-2(p+p')\cdot\bar{p}\right]}$$

equal due to energy conservation

momentum conservation

Momentum and energy conservation restrict the choice of transition probability $W(p_1, p_2 \mid p, p')$:

$$\begin{cases} p_1^2 + p_2^2 = p^2 + (p')^2 \\ p_1 + p_2 = p + p' \end{cases} \Rightarrow \|p_1 - p_2\| = \|p - p'\|$$

Which means that the <u>relative velocity</u> of colliding particles i and j, $v_{ij} = \|v_i - v_j\|$, simply <u>rotates</u> by some angle, whose probability distribution $P(\vec{\theta})$ lives on the unit sphere.

For specific models of the pairwise interaction, one can derive appropriate collision probabilities using kinetic theory. For example, for two rigid or hard spheres colliding the following is used in the Direct Simulation Monte Carlo (DSMC) method:

① $\vec{\vartheta}_{ij}$ randomly rotates with $P(\vec{\vartheta})$ uniformly distributed on the unit sphere

② $W(P_1, P_2 | P, P') \sim \|P_1 - P_2\|$ (faster particles collide more often)

With a particular choice of the collision kernel $W(p_1, p_2 / p, p')$ the Boltzmann equation is an integro-differential equation that can in principle be solved - but the dimensionality is too high for most practical computing.

Instead, do a Kinetic Monte Carlo algorithm in which we use a particle algorithm to sample a single trajectory. Think of it as a MCMC model of gas dynamics (really fluid dynamics)

To make a particle algorithm work, we need to get rid of the singular collision kernel in the Boltzmann equation (no δ functions!): this is actually more physically-realistic!

Stochastic Collision MCMC fluid model

If (while) two particles i and j are at a distance $r_{ij} = \|r_i - r_j\| \le D$, there is a Poisson process for collisions with rate:

$$\frac{\chi}{D} \cdot \frac{3\|v_i - v_j\|}{4}$$

Here { χ is the "interaction strength" (collision frequency)
D is the "interaction range" (molecular diameter)

Together they determine the overall collision rate, and together with the collision kernel $W(p_1, p_2 \mid p, p')$ they determine the physical properties of the stochastic fluid (e.g., viscosity, thermal cond.)

{ Simulating this sort of system using our usual KMC algorithm is rather difficult (discuss on board): Use splitting instead! REMEMBER VERLET!

Direct Simulation Monte Carlo:

(1) Propagate (advect) the particles by $\Delta t/2$ and sample averages.

(2) Process collisions (usual KMC) keeping particles positions fixed.
Usually one uses a sort of τ-leaping approximation in which transition rates are assumed constant and one samples the number of events to execute.

(3) Propagate by another $\Delta t/2$

Lots of algorithmic choices enter in performing the collision step:

(1) In principle one should perform collisions pair-by-pair (not parallelizable and expensive computationally)

(2) Linked-list cells are used to identify nearby particles. In traditional DSMC, only particles in the same cell are collided ($\Delta x << \lambda$ = mean free path), which leads to grid artifacts, but is much faster and simplifies the code.

(3) Often a Poisson generator is replaced with Gaussian or uniform.

Traditional DSMC algorithm

(1) Propagate particles with fixed velocities for time interval Δt, handling any boundaries.

(2) Sort particles into a grid of collision cells. Let N_c denote number of particles in cell c.

(3) For each cell (parallel):

a) Obtain a reasonably tight upper bound $\sigma_r^{max} \approx 2\sigma_{max}$

b) Select (using a uniform random number generator) from the list of particles in cell c

$$N_{coll} \sim \chi N_c^2 \, \upsilon_r^{max} \cdot \Delta t \qquad \underline{\text{trial}}$$

pairs of particles for collision

c) Accept each pair for collision with probability $p = \dfrac{\upsilon_{ij}}{\upsilon_r^{max}}$

d) Sample post-collisional velocities for the colliding particles using the collision kernel

Guidelines:

(A) Select grid size $\Delta x \ll \lambda$, mean free path

(B) Select time step $\Delta t \ll \bar{\tau}$, mean free time

Isotropic DSMC (Donev, Garcia, Alder)

1+2 are unchanged

(3) Visit the cells one by one in random order:

(a) Build a list of N_p particles in neighboring cells (including the N_c particles)

(b) Select $N_{coll} \sim \chi N_c N_p v_r^{max} \Delta t$ pairs of particles, one particle from cell c, the other from the neighbouring

(c) If the pair is closer than distance D, i.e., $r_{ij} \leq D$, do steps (e) and (d) in traditional algorithm

Traditionally, DSMC is used to model transport in rarefied gas flows (rockets), i.e., to solve the Boltzmann equation

This is a coarse-grained method!

(1) Not only is the dynamics coarse grained to be a MCMC instead of Hamiltonian

but also

(2) In a typical simulation one DSMC particle represents millions of air molecules (atoms)

[but this gives fake (large) fluctuations]

The basic ideas are a lot more general!