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OVERVIEW

Stochastic theory of direct simulation Monte Carlo method

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Abstract A treatment of direct simulation Monte Carlo method as a Markov process with a master equation is given and the corresponding master equation is derived. A hierarchy of equations for the reduced probability distributions is derived from the master equation. An equation similar to the Boltzmann equation for single particle probability distribution is derived using assumption of molecular chaos. It is shown that starting from an uncorrelated state, the system remains uncorrelated always in the limit $N\rightarrow\infty$, where N is the number of particles. Simple applications of the formalism to direct simulation money games are given as examples to the formalism. The formalism is applied to the direct simulation of homogenous gases. It is shown that appropriately normalized single particle probability distribution satisfies the Boltzmann equation for simple gases and Wang Chang–Uhlenbeck equation for a mixture of molecular gases. As a consequence of this development we derive Birds no time counter algorithm. We extend the analysis to the inhomogeneous gases and define a new direct simulation algorithm for this case. We show that single particle probability distribution satisfies the Boltzmann equation in our algorithm in the limit $N\rightarrow\infty$, $V_k\rightarrow 0$, $\Delta t\rightarrow 0$ where V_k is the volume of kth cell. We also show that our algorithm and Bird's algorithm approach each other in the limit $N_k\rightarrow\infty$ where N_k is the number of particles in the volume V_k.

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1 Introduction

Direct simulation Monte Carlo method (DSMC) [1] is a standard method to solve the Boltzmann equation numerically. In this method one divides space into cells of volume V_k ($k = 1, 2, 3,...$) and takes a large number (N) of simulated particles (10^3-10^6) to represent real gas molecules. The time evolution of the gas for a short time period Δt is calculated in two steps. In the first step some pairs of particles in the same cell are chosen randomly and are allowed to collide without changing their positions. A collision is allowed with a probability proportional to $u\Sigma$ where u is the relative velocity and Σ is the total cross-section. In the second step all particles are propagated without collisions for a time Δt.

The method is invented by Bird, and Bird introduced the method based on physical arguments. A seminal paper of Bird [2] gives somewhat heuristic arguments to justify its use to solve the Boltzmann equation. One variant of the method was derived by Nanbu [3] starting from the Boltzmann equation. Also it appears that essentially the same stochastic algorithms for a homogenous gas were invented independently by people interested in using them as a pedagogical tool to demonstrate evolution of a gas toward Maxwell-Boltzmann (MB) distribution [4–6]. In order to represent time evolution of the real gas such methods should converge to the true solution of the Boltzmann equation in the limit of $N\rightarrow\infty$, $V_k\rightarrow 0$, $\Delta t\rightarrow 0$. Convergence proofs were given by Babovsky [7] and Babovsky and Illner [8] for Nanbu's method and by Wagner [9] for Bird's method.

The cited convergence proofs are very formal and they appear to be written for mathematicians. In this paper we give a simple derivation of Birds no time counter algorithm. We also show that, in DSMC, appropriately

normalized single particle probability distribution satisfies Boltzmann equation for simple gases and Wang Chang–Uhlenbeck equation for molecular gases and their mixtures. The language of this development is familiar to the physicist from the well known BBGKY hierarchy.

The developments in the DSMC methods up to 1994 are described in Bird's book [1]. The subject is treated in some books [10–12] on rarified gas flows and numerical methods of Boltzmann equation. Although we are not aware of any recent comprehensive review paper on DSMC methods (probably numerous different applications, its many variations and hybrid methods are too much to review in a single paper), there are some reviews about particular applications and various hybrid methods. We mention two recent reviews by Bruno et al. [13] and Wu et al. [14] in this category.

In the next section we develop a general formalism for direct simulation. In order to demonstrate usefulness of the formalism we apply it to some simple money games. In Sect. 3 we apply the formalism to homogenous gases and show that, if appropriate collision kernels are chosen, the one particle probability distribution obeys the Boltzmann equation for simple gases and the Wang Chang–Uhlenbeck equation for molecular gases and their mixtures. In Sect. 4 we derive DSMC algorithm for inhomogeneous gases. Finally in the last section we give a summary and discussion.

2 Direct simulation as a Markov process

2.1 The master equation

Assume that we have an assembly of things we call 'particles'. Particles can be real particles in a gas or humans or anything you can imagine. There are N particles in the assembly where N is a very large number. Each member of the assembly can be in any one of the 'states' where states are labeled by the parameter μ. For a real gas μ can be velocity vectors and for an assembly of people μ can be the money in their pocket on bank account. The μ can be discrete or continuous and it can stand for a collection of indices that can be both continuous and discrete. For the rest of this section we will treat μ as a continuous index. Integration over μ is actually integration over the continuous indices and summation over the discrete indices that μ stands for.

In the direct simulation algorithms we play a stochastic game with this assembly. We randomly pick pairs of particles and let them 'collide'. A collision is an event that the particles change their states with a prescribed probability. The aim of this paper is to demonstrate the relations between results of such a stochastic simulation algorithm and equations governing single particle distribution such as the Boltzmann equation.

Suppose we picked particles with states μ_A and μ_B. The probability that they will end up with state labels μ_C and μ_D in the volume $\mathrm{d}\mu_C\mathrm{d}\mu_D$ is $T(\mu_A, \mu_B; \mu_C, \mu_D)\mathrm{d}\mu_C\mathrm{d}\mu_D$ where $T(\mu_A, \mu_B; \mu_C, \mu_D)$ is the collision kernel. Collision kernel is assumed to be symmetric

$$T(\mu_A, \mu_B; \mu_C, \mu_D) = T(\mu_C, \mu_D; \mu_A, \mu_B), \tag{1}$$

$$T(\mu_A, \mu_B; \mu_C, \mu_D) = T(\mu_B, \mu_A; \mu_D, \mu_C). \tag{2}$$

Also the probabilities are normalized

$$\int T(\mu_A, \mu_B; \mu_C, \mu_D)\mathrm{d}\mu_C\mathrm{d}\mu_D = \int T(\mu_A, \mu_B; \mu_C, \mu_D)\mathrm{d}\mu_A\mathrm{d}\mu_B = 1. \tag{3}$$

We define N-particle probability distribution $f^{(N)}(\mu_1, \mu_2,..., \mu_N; n)$ such that $f^{(N)}(\mu_1, \mu_2,..., \mu_N; n)\mathrm{d}\mu_1\mathrm{d}\mu_2,..., \mathrm{d}\mu_N$ is the probability of finding the particles 1, 2,..., N in the $\mathrm{d}\mu_1\mathrm{d}\mu_2,..., \mathrm{d}\mu_N$ phase space volume after the nth collision. Since the particles are identical the $f^{(N)}(\mu_1, \mu_2,..., \mu_N; n)$ is assumed to be completely symmetric

$$f^{(N)}(\mu_1, \ldots, \mu_j, \ldots, \mu_i, \ldots, \mu_N; n) = f^{(N)}(\mu_1, \ldots, \mu_i, \ldots, \mu_j, \ldots, \mu_N; n). \tag{4}$$

We define reduced M-particle distribution as

$$f^{(M)}(\mu_1, \ldots, \mu_M; n) = \int f^{(N)}(\mu_1, \ldots, \mu_N; n)\mathrm{d}\mu_{M+1} \mathrm{d}\mu_{M+2}, \ldots, \mathrm{d}\mu_N. \tag{5}$$

We will denote $f^{(M)}(\mu_1,..., \mu_M; n)$ $(M = 1, 2,..., N)$ as $f^{(M)}(\mu; n)$ shortly. As a convenient notation we also define $f_{ij}^{(M)}(\mu_A, \mu_B; n)$ as

$$f_{ij}^{(M)}(\mu_A, \mu_B; n) = f^{(M)}(\mu_1, \ldots, \mu_i = \mu_A, \ldots, \mu_{j=}\mu_B, \ldots, \mu_M; n), \tag{6}$$

where μ_i and μ_j are replaced with μ_A and μ_B in $f^{(M)}(\mu_1,..., \mu_M; n)$. Examples are

$$f_{31}^{(N)}(\mu_A, \mu_B; n) = f(\mu_B, \mu_2, \mu_A, \mu_4, \ldots, \mu_N; n) \tag{7}$$

$$f_{24}^{(N)}(\mu_A, \mu_B; n) = f(\mu_1, \mu_A, \mu_3, \mu_B, \mu_5, \ldots, \mu_N; n). \tag{8}$$

We are ready to start now. The equation satisfied by the $f^{(N)}(\mu\ ; n)$ is given by

$$f^{(N)}(\mu; n+1) = \frac{1}{N(N-1)} \sum_{i=1}^{N} \sum_{j\neq i}^{N} \int f_{ij}^{(N)}(\mu_A, \mu_B; n) \times T(\mu_A, \mu_B; \mu_i, \mu_j)\mathrm{d}\mu_A\mathrm{d}\mu_B. \tag{9}$$

The meaning of this equation is clear. If the last pair we collided is i, j molecules, the probability of having μ_i, μ_j pairs at the end of collision is the probability of having initial

states μ_A, μ_B [represented by $f_{ij}^{(N)}(\mu_A, \mu_B; n)\mathrm{d}\mu_A\mathrm{d}\mu_B$] multiplied by the probability of ending with μ_i, μ_j [represented by $T(\mu_A, \mu_B; \mu_i, \mu_j)$]. The sum over i, j and the factor $1/N(N-1)$ takes care of the fact that all pairs (respecting order of the molecules) are possible with the probability $1/N(N-1)$. The state of the system after $n+1$ collisions depends on the state of system after n collisions and the direct simulation game is a Markov process actually. Equation 9 is the master equation for this stochastic process.

In order to see clearly how this equation is derived let us multiply this with $\mathrm{d}\mu_1\mathrm{d}\mu_2$,..., $\mathrm{d}\mu_N$. The left hand side is

$$f^{(N)}(\mu; n+1)\mathrm{d}\mu_1\mathrm{d}\mu_2, \ldots, \mathrm{d}\mu_N \tag{10}$$

and it is the probability of the system being in the phase space volume $\mathrm{d}\mu_1\mathrm{d}\mu_2$,..., $\mathrm{d}\mu_N$ after the $(n+1)$th collision. On the right side we have

$$\frac{1}{N(N-1)}\sum_{i=1}^{N}\sum_{j\neq i}^{N}\int f_{ij}^{(N)}(\mu_A, \mu_B; n)T(\mu_A, \mu_B; \mu_i, \mu_j) \times \mathrm{d}\mu_A\mathrm{d}\mu_B\mathrm{d}\mu_1\mathrm{d}\mu_2\ldots, \mathrm{d}\mu_N. \tag{11}$$

Here the integration is over μ_A and μ_B only. In order to interpret this let us look at $i=1$ and $j=2$ term. It is the following term

$$\left[\frac{1}{N(N-1)}\right]\left[f^{(N)}(\mu_A, \mu_B, \mu_3, \mu_4, \ldots, \mu_N) \times \mathrm{d}\mu_A\mathrm{d}\mu_B\mathrm{d}\mu_3\mathrm{d}\mu_4, \ldots, \mathrm{d}\mu_N\right] \times \left[T(\mu_A, \mu_B; \mu_1, \mu_2)\mathrm{d}\mu_1\mathrm{d}\mu_2\right] \tag{12}$$

integrated over μ_A, μ_B. In this form the terms under the integration are product of three probabilities. $1/N(N-1)$ is the probability of choosing $i=1, j=2$ pairs. The second parenthesis is the probability of finding the system in $\mathrm{d}\mu_A\mathrm{d}\mu_B\mathrm{d}\mu_3\mathrm{d}\mu_4$,..., $\mathrm{d}\mu_N$ phase space volume before the collision. The last parenthesis is the probability of taking particles one and two from $\mathrm{d}\mu_A\mathrm{d}\mu_B$ to $\mathrm{d}\mu_1\mathrm{d}\mu_2$ interval after the collision. When integrated over μ_A, μ_B this term becomes the probability of arriving in $\mathrm{d}\mu_1\mathrm{d}\mu_2$,..., $\mathrm{d}\mu_N$ phase space volume after $(n+1)$th collision via a collision between particles one and two. If all such term are summed over i and j we find the probability of arriving in $\mathrm{d}\mu_1\mathrm{d}\mu_2$,..., $\mathrm{d}\mu_N$ phase space volume after $(n+1)$th collision which is the same as Eq. 10.

2.2 Asymptotic behavior of the master equation

Let us introduce a short notation for state variables:

$$\begin{aligned} X &= (x_1, x_2, \ldots, x_N) \quad \mathrm{d}X = \mathrm{d}x_1\mathrm{d}x_2\ldots, \mathrm{d}x_N \\ Y &= (y_1, y_2, \ldots, y_N) \quad \mathrm{d}Y = \mathrm{d}y_1\mathrm{d}y_2\ldots, \mathrm{d}y_N \\ Z &= (z_1, z_2, \ldots, z_N) \quad \mathrm{d}Z = \mathrm{d}z_1\mathrm{d}z_2\ldots, \mathrm{d}z_N. \end{aligned} \tag{13}$$

Then the master equation can be written in the form

$$f(X; n+1) = \int P(X, Y)f(Y; n)\mathrm{d}Y. \tag{14}$$

The $P(X,Y)$ has $N(N-1)$ terms and each one of the terms contains $N-2$ delta functions. For example $i=1, j=2$ term reads as

$$\frac{1}{N(N-1)}T(x_1, x_2; y_1, y_2)\delta(x_3 - y_3)\ldots\delta(x_N - y_N). \tag{15}$$

The general expression for $P(X,Y)$ is

$$P(X,Y) = \frac{1}{N(N-1)}\sum_{i=1}^{N}\sum_{j\neq i}^{N}\left(T(x_i, x_j; y_i, y_j)\prod_{k\neq i,j}^{N}\delta(x_k - y_k)\right). \tag{16}$$

The $P(X,Y)\mathrm{d}X$ is the probability that the system jumps from Y to $\mathrm{d}X$ phase space volume after a collision. As can be seen directly from Eq. 16 it is also symmetric: $P(X,Y) = P(Y,X)$. As a probability density it satisfies the normalization condition

$$\int P(X, Y)\mathrm{d}X = \int P(X, Y)\mathrm{d}Y = 1. \tag{17}$$

We will need convolution of $P(X,Y)$ shortly. Let us define $W(X,Y)$ as

$$W(X, Y) = \int P(X, Z)P(Y, Z)\mathrm{d}Z. \tag{18}$$

It is easily seen that $W(X,Y)$ is symmetric ($W(X,Y) = W(Y,X)$) and it also satisfies a normalization condition

$$\int W(X, Y)\mathrm{d}X = \int W(X, Y)\mathrm{d}Y = 1. \tag{19}$$

Now we are ready to discuss asymptotic behavior or the master equation. Let us form $\int f^2(X; n+1)\mathrm{d}X$ as

$$\int f^2(X; n+1)\mathrm{d}X = \int\left(\int P(X, Y)f(Y; n)\mathrm{d}Y\right) \times \left(\int P(X, Z)f(Z; n)\mathrm{d}Z\right)\mathrm{d}X \tag{20}$$

$$= \int W(Y, Z)f(Y; n)f(Z; n)\mathrm{d}Y\mathrm{d}Z. \tag{21}$$

We can also write $\int f^2(X; n)\mathrm{d}X$ as

$$\int f^2(X; n)\mathrm{d}X = \int W(Y, Z)f^2(Y)\mathrm{d}Y\mathrm{d}Z = \int W(Y, Z)f^2(Z)\mathrm{d}Y\mathrm{d}Z \tag{22}$$

which follows from Eq. 19. Using these two relations we can write the following

$$\int f^2(X;n+1)\mathrm{d}X - \int f^2(X;n)\mathrm{d}X$$
$$= \int W(Y,Z)f(Y;n)f(Z;n)\mathrm{d}Y\mathrm{d}Z$$
$$-\frac{1}{2}\int W(Y,Z)f^2(Y)\mathrm{d}Y\mathrm{d}Z$$
$$-\frac{1}{2}\int W(Y,Z)f^2(Z)\mathrm{d}Y\mathrm{d}Z. \quad (23)$$

The right side can be written as

$$\int f^2(X;n+1)\mathrm{d}X - \int f^2(X;n)\mathrm{d}X$$
$$= -\frac{1}{2}\int W(Y,Z)(f(Y;n)-f(Z;n))^2\mathrm{d}Y\mathrm{d}Z. \quad (24)$$

Since $W(Y,Z)$ is always nonnegative the expression on the right is always negative or zero. This means $\int f^2(X;n)\mathrm{d}X$ decreases after each collision. The decrease stops when $f(Y;n) - f(Z;n) = 0$ for all Y and Z, and this means $f(X;n)$ must be a constant. The equilibrium is reached when $f(X;n)$ is microcanonical distribution.

There is a final point to be discussed here. The above argument proves that the probability density in the direct simulation always converges towards microcanonical distribution. If the phase space is divided in separate regions such that collisions cannot take the system from one region to another then the above argument must be modified. If Y and Z belong to different regions then $W(Y,Z) = 0$ and $f(Y;n) - f(Z;n) = 0$ is not required. But if Y and Z belong to the same region then $W(Y,Z) \neq 0$ and $f(Y;n) - f(Z;n) = 0$ is required. This means that $f(X;n)$ must be a constant in each region asymptotically but they can be different constants. For direct simulation of a gas total energy and total momentum are conserved, and the system stays on a constant total energy-total momentum shell. Asymptotically the $f(X;n)$ will be constant on each shell but they will be different constant for different shells.

2.3 The hierarchy of reduced probability distributions

If we integrate the master equation over $\mathrm{d}\mu_{M+1}$, μ_{M+2},..., μ_N we obtain the equation

$$f^{(M)}(\mu;n+1) = \frac{(N-M)(N-M-1)}{N(N-1)}f^{(M)}(\mu;n)$$
$$+\frac{2(N-M)}{N(N-1)}\sum_{i=1}^{M}\int f_{i,M+1}^{(M+1)}(\mu_A,\mu_B;n)$$
$$\times T(\mu_A,\mu_B;\mu_i,\mu_C)\mathrm{d}\mu_A\mathrm{d}\mu_B\mathrm{d}\mu_C$$
$$+\frac{M(M-1)}{N(N-1)}\sum_{i=1}^{M}\sum_{j\neq i}^{M}\int f_{i,j}^{(M)}(\mu_A,\mu_B;n)$$
$$\times T(\mu_A,\mu_B;\mu_i,\mu_j)\mathrm{d}\mu_A\mathrm{d}\mu_B. \quad (25)$$

The $f^{(M)}(\mu;n+1)$ depends on $f^{(M+1)}(\mu;n)$ and this represents a hierarchy of equations similar to the well-known BBGKY hierarchy [15].

The first equation in the hierarchy is

$$f^{(1)}(\mu;n+1) = (1-2/N)f^{(1)}(\mu;n)$$
$$+\frac{2}{N}\int f^{(2)}(\mu_A,\mu_B;n)T(\mu_A,\mu_B;\mu_C,\mu)$$
$$\times \mathrm{d}\mu_A\mathrm{d}\mu_B\mathrm{d}\mu_C. \quad (26)$$

If we make the assumption of molecular chaos (AMC)

$$f^{(2)}(\mu_A,\mu_B;n) = f^{(1)}(\mu_A;n)f^{(1)}(\mu_B;n), \quad (27)$$

we obtain a nonlinear equation for $f^{(1)}(\mu;n)$ similar to the Boltzmann equation.

From now on we will suppress the superscript (1) in $f^{(1)}(\mu;\tau)$ wherever it does not cause confusion. Using the relation

$$f(\mu,n) = \int f(\mu,n)f(\mu_C,n)T(\mu_A,\mu_B;\mu_C,\mu)\mathrm{d}\mu_A\mathrm{d}\mu_B\mathrm{d}\mu_C, \quad (28)$$

which follows from Eq. 3 and the normalization of $f(\mu_C)$ and imposing the assumption of molecular chaos we can write Eq. 26 as

$$f(\mu;n+1) = f(\mu;n)$$
$$+\frac{2}{N}\int [f,f]T(\mu_A,\mu_B;\mu_C,\mu)\mathrm{d}\mu_A\mathrm{d}\mu_B\mathrm{d}\mu_C \quad (29)$$

$$[f,f] = f(\mu_A,n)f(\mu_B,n) - f(\mu_C,n)f(\mu,n). \quad (30)$$

A second simplification occurs for large N. The $2/N$ appearing in Eq. 29 is a small number and we can take $\tau = 2n/N$ as a continuous parameter which we call the collision time. Then $\Delta\tau = 2/N$ and $[f(\mu;n+1) - f(\mu;n)]/\Delta\tau$ can be taken as $\partial f(\mu;\tau)/\partial\tau$. The Eq. 29 can be written in either of the following forms:

$$\frac{\partial f(\mu,\tau)}{\partial\tau} = \int [f,f]T(\mu_A,\mu_B;\mu_C,\mu)\mathrm{d}\mu_A\mathrm{d}\mu_B\mathrm{d}\mu_C. \quad (31)$$

$$\frac{\partial f(\mu,\tau)}{\partial\tau} = -f(\mu) + \int f(\mu_A)f(\mu_B)T(\mu_A,\mu_B;\mu_C,\mu)\mathrm{d}\mu_A\mathrm{d}\mu_B\mathrm{d}\mu_C. \quad (32)$$

We will call the first equation in the hierarchy 'the first equation' briefly for the rest of the paper. In latter parts of this paper we will call the integral on the right side of Eq. 31, 'the collision integral'. From now on we will also suppress the collision time τ in $f(\mu,\tau)$ wherever it is convenient.

2.4 Justification of assumption of molecular chaos

The only thing in this paper that is not fully rigorous is the assumption of molecular chaos. In order to have assumption of molecular chaos valid from the beginning we must start from an uncorrelated state

$$f^{(N)}(\mu_1,\mu_2,\ldots,\mu_N;n=0)=h(\mu_1)h(\mu_2)\ldots h(\mu_N), \tag{33}$$

which is what is done in direct simulations mostly. The master equation (Eq. 9) should be used to justify AMC. For finite N, the AMC is not strictly valid and the AMC should get better and better as $N\to\infty$. For $M/N \ll 1$ the Eq. 25 is written as

$$\begin{aligned} f^{(M)}(\mu;n+1) &= (1-2M/N)f^{(M)}(\mu;n)+O(1/N^2) \\ &\quad +\frac{2}{N}\sum_{i=1}^{M}\int f_{i,M+1}^{(M+1)}(\mu_A,\mu_B;n) \\ &\quad \times T(\mu_A,\mu_B;\mu_i,\mu_C)\mathrm{d}\mu_A\mathrm{d}\mu_B\mathrm{d}\mu_C \end{aligned} \tag{34}$$

where $O(1/N^2)$ are the terms of order $1/N^2$. If we invoke collision time $\tau = 2n/N$ again and write $[f^{(M)}(\mu;n+1) - f^{(M)}(\mu;n)]/\Delta\tau = \partial f^{(M)}(\mu;\tau)/\partial\tau$ and we take the limit $N\to\infty$ we obtain

$$\begin{aligned} \frac{\partial f^{(M)}(\mu;\tau)}{\partial\tau} &= -Mf^{(M)}(\mu;\tau)+\sum_{i=1}^{M}\int f_{i,M+1}^{(M+1)}(\mu_A,\mu_B;\tau) \\ &\quad \times T(\mu_A,\mu_B;\mu_i,\mu_C)\mathrm{d}\mu_A\mathrm{d}\mu_B\mathrm{d}\mu_C \end{aligned} \tag{35}$$

where $M = 1, 2,\ldots, \infty$. This is an infinite chain of coupled differential equations. If we invoke

$$f^{(M)}(\mu_1,\mu_2,\ldots,\mu_M;\tau)=f^{(1)}(\mu_1;\tau)f^{(1)}(\mu_2;\tau)\ldots f^{(1)}(\mu_M;\tau). \tag{36}$$

in the Eq. 35, all the equations in the infinite chain are satisfied, provided $f^{(1)}(\mu;\tau)$ satisfies Eq. 31. This proves that in the limit $N\to\infty$ the AMC remains valid for all τ if we start from an uncorrelated initial state.

What happens if we start from a correlated state that does not satisfy AMC? For finite N there are always some correlations to any order. We know that the system evolves towards microcanonical distribution. In the limit $N\to\infty$ microcanonical distribution obeys AMC. This means even if we start from a correlated state the system will satisfy AMC better and better as the system evolves towards equilibrium for large N. Collisions destroy correlations. It should take only a few collisions per particle to destroy initial correlations. Moreover, in the practical applications of DSMC in gas dynamics the N is almost always large and initial state is chosen as almost uncorrelated from the beginning. Therefore, using the first equation to determine the single particle probability density is a justifiable process.

2.5 Collision invariants and the H-theorem

Since our collision kernel has the same symmetries as the collision integral in the Boltzmann equation, many results that follow from those symmetries in Boltzmann equation are valid for direct simulation too. In particular, we mention conservation of collision invariants and the H-theorem.

Consider a collision that first particle enters with μ_A and the second particle enters with μ_B. The final states of the first and second particles are μ_C and μ_D. Consider a function $g(\mu)$ of the state variable μ. The $g(\mu)$ is a collision invariant if

$$\Delta g = g(\mu_D)+g(\mu_C)-g(\mu_A)-g(\mu_B)=0 \tag{37}$$

in all collisions allowed by the kernel $T(\mu_A, \mu_B; \mu_C, \mu_D)$. For a real gas without internal degrees of freedom the μ stands for the velocity components V_X, V_Y, V_Z of a molecule. Momentum and kinetic energies are conserved in collisions. Then $g_1(\mu) = mV_X$, $g_2(\mu) = mV_Y$, $g_3(\mu) = mV_Z$, $g_4(\mu) = m(V_X^2+V_Y^2+V_Z^2)/2$ are collision invariants. If particles are humans playing a money game then μ is the money in their pocket. Since the total money is conserved in gambling we have $\mu_D+\mu_C-\mu_A-\mu_B=0$ which means $g(\mu)=\mu$ is a collision invariant.

Given a collision invariant $g(\mu)$, using symmetries of $T(\mu_A, \mu_B; \mu_C, \mu)$, it can be shown easily that the 'time' derivation of the average $\langle g(\mu)\rangle$ vanishes

$$\frac{\mathrm{d}}{\mathrm{d}\tau}\langle g(\mu)\rangle = \frac{\mathrm{d}}{\mathrm{d}\tau}\int f(\mu,\tau)g(\mu)\mathrm{d}\mu = 0. \tag{38}$$

Derivation is parallel to the Boltzmann equation case and need not be detailed.

We can derive an H-theorem for the first equation. Defining $H(\tau)$ a

$$H(\tau)=\int f(\mu)\ln(f(\mu))\mathrm{d}\mu, \tag{39}$$

and using the Eqs. 1, 2 and 31 we can show that

$$\frac{\mathrm{d}H}{\mathrm{d}\tau}\le 0. \tag{40}$$

The derivation is entirely similar to the Boltzmann equation case and it is omitted. There are two possibilities here. The H keeps decreasing toward negative infinity or it approaches an absolute minimum asymptotically and the system approaches toward an equilibrium distribution. Following the usual arguments of the H-theorem, the decrease of H stops only when

$$\ln f(\mu_A) + \ln f(\mu_B) = \ln f(\mu_C) + \ln f(\mu), \tag{41}$$

is satisfied which implies that $\ln f(\mu)$ is a collision invariant. If we choose the $T(\mu_A, \mu_B; \mu_C, \mu)$ such that there are collision invariants $g_i(\mu)$ $(i = 1, 2,..., L)$ then $\ln f(\mu)$ must be expressible as a linear combinations of these collision invariants as

$$\ln f(\mu) = c_1 g_1(\mu) + c_2 g_2(\mu) + \cdots + c_L g_L(\mu), \tag{42}$$

where $c_1,..., c_L$ are parameters describing the equilibrium.

There is at least one trivial collision invariant. It is the number of particles entering and exiting the collision which corresponds to $g_1(\mu) = 1$. When there are additional collision invariants the H has a lower bound usually. For the case of real gases, momentum and energy are collision invariants and this makes H bounded from below.

2.6 Example: a game of discrete money gambling

Here, we give a simple example of a direct simulation money game with finite number of discrete states. Suppose everybody is given some random amount of money at the beginning. Everybody in the assembly has 1, 2 or 3$ in their pocket. The random assignment of initial money ensures assumption of molecular chaos from the beginning. The collisions take place as follows: player 1 and player 2 share their total money such that nobody gets more than 3$ and both players get at least 1$. All the possibilities satisfying these conditions have equal probabilities. If they have total 2$ (1$ each) then the only possibility is that they will have 1$ each at the end with unity probability. If they have total 3$ then the possible outcomes are (1,2) and (2,1) with equal 1/2 probabilities. If they have total 4$ then possible outcomes are (1,3), (3,1), (2,2) with 1/3 probability each. If they have total 5$ then possible outcomes are (2,3) and (3,2) with 1/2 probability each. Finally if they have total 6$ (3$ each) then the only possibility is (3,3) with unity probability.

For this game the money is conserved in collisions, and only transitions between states with equal amount of total money is possible. For N particles the total money can have values between N and $3N$, and there are a total of $2N + 1$ separate regions in phase space. One cannot cross from one to another of these regions by making collisions.

Now that we defined the game, how does single particle distribution evolves as we make collisions? The state variable μ is the amount of the money in the persons pocket and it takes the values 1, 2, 3. Let $P_\mu(\tau)$ be the probability that a chosen person will have the money μ at the collision time τ. From Eq. 32 the $P_\mu(\tau)$ satisfies

$$\begin{aligned}\frac{dP_1}{d\tau} = &- P_1 + P_1^2 T(1,1,1,1) + P_1 P_2 T(1,2;2,1) \\ &+ P_2 P_1 T(2,1;2,1) + P_1 P_3 T(1,3;3,1) \\ &+ P_3 P_1 T(3,1;3,1) + P_2 P_2 T(2,2;2,1),\end{aligned} \tag{43}$$

$$\begin{aligned}\frac{dP_2}{d\tau} = &- P_2 + P_2^2 T(2,2,2,2) \\ &+ P_1 P_2 T(1,2;1,2) + P_2 P_1 T(2,1;1,2) \\ &+ P_1 P_3 T(1,3;2,2) + P_3 P_1 T(3,1;2,2) \\ &+ P_2 P_3 T(2,3;3,2) + P_3 P_2 T(3,2;3,2),\end{aligned} \tag{44}$$

and

$$\begin{aligned}\frac{dP_3}{d\tau} = &- P_3 + P_1 P_3 T(1,3;1,3) + P_3 P_1 T(3,1;1,3) \\ &+ P_3^2 T(3,3;3,3) + P_2 P_3 T(2,3;2,3) \\ &+ P_3 P_2 T(3,2;2,3) + P_2^2 T(2,2,1,3).\end{aligned} \tag{45}$$

Inserting the T values this can be written as

$$\frac{dP_1}{d\tau} = -P_1 + P_1^2 + P_1 P_2 + \frac{2}{3} P_1 P_3 + \frac{1}{3} P_2^2, \tag{46}$$

$$\frac{dP_2}{d\tau} = -P_2 + \frac{1}{3} P_2^2 + P_1 P_2 + \frac{2}{3} P_1 P_3 + P_2 P_3, \tag{47}$$

$$\frac{dP_3}{d\tau} = -P_3 + \frac{2}{3} P_1 P_3 + P_2 P_3 + P_3^2 + \frac{1}{3} P_2^2. \tag{48}$$

This is a complicated set of nonlinear differential equations. But there are simplifying features because we know the collision invariants $g_1(\mu) = 1$ and $g_2(\mu) = \mu$. Summing the Eqs. 46–48 we obtain

$$\frac{d}{d\tau}(P_1 + P_2 + P_3) = (P_1 + P_2 + P_3 - 1)(P_1 + P_2 + P_3), \tag{49}$$

and

$$\frac{d}{d\tau}(P_1 + 2P_2 + 3P_3) = (P_1 + P_2 + P_3 - 1)(P_1 + 2P_2 + 3P_3). \tag{50}$$

The first equation tells us that since $P_1 + P_2 + P_3 = 1$ at the beginning it always remains unity and probability is conserved. The second equation tells us that since $P_1 + P_2 + P_3 - 1 = 0$ always the expectation value $\langle \mu \rangle = P_1 + 2P_2 + 3P_3$ is conserved.

We denote expected money in the pocket with m. We have two equations

$$P_1 + P_2 + P_3 = 1, \tag{51}$$

$$P_1 + 2P_2 + 3P_3 = m, \tag{52}$$

from which we solve P_2 and P_3 as

$$P_2 = -2P_1 + 3 - m, \tag{53}$$

$$P_3 = P_1 + m - 2. \tag{54}$$

Inserting P_2 and P_3 in the Eq. 46 we obtain

$$\frac{dP_1}{d\tau} = P_1^2 + (m - \frac{10}{3})P_1 + \frac{1}{3}(3-m)^2. \tag{55}$$

Calculating roots of the quadratic term on the right we write this as

$$\frac{dP_1}{d\tau} = (P_1 - r_1)(P_1 - r_2), \tag{56}$$

where r_1 and r_2 are

$$r_1 = \frac{1}{6}\left(10 - 3m + \sqrt{1 + 3(m-1)(3-m)}\right), \tag{57}$$

$$r_2 = \frac{1}{6}\left(10 - 3m - \sqrt{1 + 3(m-1)(3-m)}\right). \tag{58}$$

Notice that since $1 \le m \le 3$ the term under the square root is always greater than or equal to unity.

Solving Eq. 56 is straightforward and we obtain

$$P_1(\tau) = \frac{r_2(p_0 - r_1) - r_1(p_0 - r_2)e^{-\lambda\tau}}{(p_0 - r_1) - (p_0 - r_2)e^{-\lambda\tau}}, \tag{59}$$

where $p_0 = P_1(\tau = 0)$ and $\lambda = r_1 - r_2$. It is easy to verify that $P_1(\infty) = r_2$ and $P_1(\tau)$ approaches this limit exponentially fast. One can check from Eq. 58 that $r_2 = 1$ at $m = 1$ and $r_2 = 0$ at $m = 3$ and it behaves as it is expected.

The conditions $0 \le P_2 \le 1$ and $0 \le P_3 \le 1$ together with Eqs. 53 and 54 gives conditions that $P_1(\tau)$ must satisfy. These conditions are expressed as $2 - m \le P_1 \le (3-m)/2$ when $m \le 2$ and $0 \le P_1 \le (3-m)/2$ when $m > 2$. Therefore, $P_1(\tau = 0)$ initial value should obey these limitations.

To find the equilibrium distribution directly without solving the differential equation we set $dP_\mu/d\tau = 0$ for $\mu = 1, 2, 3$ in Eqs. 46–48, and we obtain a set of algebraic nonlinear equations

$$-P_1 + P_1^2 + P_1P_2 + \frac{2}{3}P_1P_3 + \frac{1}{3}P_2^2 = 0 \tag{60}$$

$$-P_2 + \frac{1}{3}P_2^2 + P_1P_2 + \frac{2}{3}P_1P_3 + P_2P_3 = 0 \tag{61}$$

$$-P_3 + \frac{2}{3}P_1P_3 + P_2P_3 + P_3^2 + \frac{1}{3}P_2^2 = 0. \tag{62}$$

Setting $P_1 = a$, $P_2 = ab$, $P_3 = ab^2$ all three equations are satisfied provided the normalization condition

$$a(1 + b + b^2) = 1, \tag{63}$$

holds. We were able to guess this solution from the H-theorem. There are two collision invariants $g_1 = 1$ and $g_2(\mu) = \mu$. The second one is a result of conservation of money in the collisions. Therefore, according to the H-theorem we must have $\ln P_\mu = C_1 + C_2\mu$ and this gives the solution $P_\mu = ab^{\mu-1}$. We need one more relation to determine both a and b. This comes from expected money in the pocket:

$$m = a\left(1 + 2b + 3b^2\right), \tag{64}$$

which is a conserved quantity during the 'time' evolution, and it is set by the initial conditions. Solving these two equation we obtain

$$a = \frac{1}{6}\left(10 - 3m - \sqrt{1 + 3(m-1)(3-m)}\right),$$
$$b = \left(m - 2 + \sqrt{1 + 3(m-1)(3-m)}\right)/2(3-m). \tag{65}$$

Notice that $a = r_2$ and this agrees with solution of the differential equation.

The H-function

$$H = P_1 \ln P_1 + P_2 \ln P_2 + P_3 \ln P_3, \tag{66}$$

is bounded from below for this problem since the function $x \ln x$ is bounded from below and $0 \le P_\mu \le 1$. We minimize H with the constraint that the expected money is fixed and probabilities are normalized. The constraints can be adopted with Lagrange multipliers. Taking the auxiliary function

$$\Psi = P_1 \ln P_1 + P_2 \ln P_2 + P_3 \ln P_3 - \lambda_2(P_1 + P_2 + P_3 - 1) - \lambda_2(P_1 + 2P_2 + 3P_3 - m)\,, \tag{67}$$

and setting $\partial\Psi/\partial P_1 = \partial\Psi/\partial P_2 = \partial\Psi/\partial P_3 = 0$ we obtain the same solution $P_\mu = ab^{\mu-1}$ where a and b satisfies the Eqs. 63 and 64. The minimum value of H becomes

$$H = a \ln a + ab \ln ab + ab^2 \ln ab^2 = \ln(ab^{m-1}). \tag{68}$$

2.7 Example 2: a game of continuous money gambling

Here, we give another example of direct simulation money games with continuous states. In this case we were not even able to solve one particle probability distribution. We just find the equation for one particle distribution and guess the stationary one particle distribution from the H-theorem. We then show that it satisfies the equation for single particle probability equation.

This time initially we give players a random amount of money between 0 and, say, 10$. Suppose we pick a pair to collide. Player 1 has μ_1 and player 2 has μ_2 amount of money. A computer produces a random number p between 0 and 1. Player 1 takes $p(\mu_1 + \mu_2)$ and player 2 takes $(1-p)(\mu_1 + \mu_2)$ amounts of money and we pick another pair to collide. What is the final distribution when the system comes to equilibrium?

The probability distribution that a person will have money μ satisfies the Eq. 32

$$\frac{\partial f(\mu)}{\partial \tau} = -f(\mu) + \int_0^\infty \mathrm{d}a \int_0^\infty \mathrm{d}b f(a) f(b) T(a,b,\mu,v) \mathrm{d}a \mathrm{d}b \mathrm{d}v, \tag{69}$$

where the collision kernel is

$$T(a,b,\mu,v) = \frac{1}{a+b}\delta(a+b-\mu - v)\Theta(a)\Theta(b)\Theta(\mu)\Theta(v). \tag{70}$$

Here $\Theta(x)$ is the standard step function

$$\Theta(x) = \begin{cases} 0 & x<0 \\ 1 & x \geq 0 \end{cases}. \tag{71}$$

If we insert the $T(a, b, \mu, v)$ given in the Eq. 70 into the Eq. 69 and perform the v integral we obtain

$$\frac{\partial f(\mu)}{\partial \tau} = -f(\mu) + \int_0^\infty \mathrm{d}a \int_0^\infty \mathrm{d}b \Theta(a+b-\mu)\frac{f(b)f(a)}{a+b}. \tag{72}$$

This can be further simplified by changing variables $x = a + b$ and $y = a$ which yields

$$\frac{\partial f(\mu)}{\partial \tau} = -f(\mu) + \int_\mu^\infty \mathrm{d}x \int_0^x \mathrm{d}y \frac{f(y)f(x-y)}{x}. \tag{73}$$

The H-theorem insures that this equation will converge to an equilibrium distribution as $\tau \to \infty$. Since we have money conservation in the collisions there are two collision invariants $g_1(\mu) = 1$ and $g_2(\mu) = \mu$. Then the equilibrium distribution is

$$f_{eq}(\mu) = Ae^{-B\mu}. \tag{74}$$

If the average money initially given to each person is m, the $f(\mu)$ should satisfy two conditions

$$\int_0^\infty f(\mu)\mathrm{d}\mu = 1, \tag{75}$$

$$\int_0^\infty \mu f(\mu)\mathrm{d}\mu = m, \tag{76}$$

and they fix the values of A and B in the Eq. 74. The solution is

$$f_{eq}(\mu) = \frac{1}{m}e^{-\mu/m}. \tag{77}$$

If we insert this solution into Eq. 73 we can easily check that right side of the equation becomes zero which confirms that $f_{eq}(\mu)$ is the equilibrium distribution.

3 Application of the direct simulation formalism to homogenous gases

3.1 Center of mass frame

In the following sections we will need some results from studying the collision in the center of mass frame. Instead of deriving them for each case separately we derive the relevant results once for the most general case in this subsection, and refer to formulae derived here as needed in the following subsections. In the rest of the paper bold letters denote vector quantities.

Particles with states $\mu_A = \mathbf{v}_A$ and $\mu_B = \mathbf{v}_B$ and enter the collision and particles with states $\mu_C = \mathbf{v}_C$ and $\mu_D = \mathbf{v}$ exit the collision. We define the center of mass (CM) coordinates as

$$\mathbf{H} = (m_A\mathbf{v}_A + m_B\mathbf{v}_B)/(m_A + m_B) \tag{78}$$

$$\mathbf{H}' = (m_A\mathbf{v}_C + m_B\mathbf{v})/(m_A + m_B), \tag{79}$$

and

$$\begin{array}{lll} \mathbf{u} = \mathbf{v}_A - \mathbf{v}_B, & u = |\mathbf{u}|, & \mathbf{n} = \mathbf{u}/u \\ \mathbf{u}' = \mathbf{v}_C - \mathbf{v}, & u' = |\mathbf{u}'|, & \mathbf{n}' = \mathbf{u}'/u' \end{array} \tag{80}$$

where m_A is the mass of particles A and C and m_B is the mass of particles B and D. For one kind of gas all masses are equal and formulae for CM velocities $\mathbf{H}$ and $\mathbf{H}'$ reduce to

$$\mathbf{H} = (\mathbf{v}_A + \mathbf{v}_B)/2, \quad \mathbf{H}' = (\mathbf{v}_C + \mathbf{v})/2. \tag{81}$$

Integrations over $\mathbf{v}_A$ and $\mathbf{v}_B$ can be carried over in the variables $\mathbf{H}$ and $\mathbf{u}$. The transformation between these two sets of variables are linear and the Jacobian is unity. Therefore

$$\int f(\mathbf{v}_A, \mathbf{v}_B)\mathrm{d}^3\mathbf{v}_A\mathrm{d}^3\mathbf{v}_B = \int f(\mathbf{H}, \mathbf{u})\mathrm{d}^3\mathbf{H}\mathrm{d}^3\mathbf{u}. \tag{82}$$

In the following subsections we will deal with integrations over $\mathbf{v}_A$, $\mathbf{v}_B$, $\mathbf{v}_C$. Integrations over $\mathbf{v}_A$, $\mathbf{v}_B$ will be converted to integration over $\mathbf{H}$ and $\mathbf{u}$ in the CM frame. In each case there will be a Dirac delta function removing the integral over $\mathbf{H}$. Integration over $\mathbf{v}_C$ will be converted to integration over $\mathbf{u}'$ since $\mathbf{v}_C = \mathbf{u}' + \mathbf{v}$ and there is no integration over $\mathbf{v}$. Furthermore, integrations over $\mathbf{u}'$ will be carried in spherical coordinates as

$$\int f(\mathbf{u}')\mathrm{d}^3\mathbf{u}' = \int f(\mathbf{u}')(u')^2\mathrm{d}u'\mathrm{d}\mathbf{n}' \tag{83}$$

and in each case there will be a Dirac delta function removing the integration over u'. In the final expressions the integration over solid angle $\mathbf{n}'$ and $\mathbf{u}$ remain at the end.

In order to evaluate the integrals we will encounter in the following subsections we must express $\mathbf{v}_A, \mathbf{v}_B, \mathbf{v}_C$ in terms of the variables $\mathbf{v}, \mathbf{u}, \mathbf{n}'$. This is a simple exercise in

collision kinetics. We will do this for the inelastic collisions with unequal masses. This is the most general case we will deal in this paper. We will assume that molecules have internal energies $\varepsilon(A)$, $\varepsilon(B)$ and $\varepsilon(C)$, $\varepsilon(D)$. Let $\epsilon = \varepsilon(A) + \varepsilon(B)$ and $\epsilon' = \varepsilon(C) + \varepsilon(D)$. From energy conservation we have $u'(u) = \sqrt{u^2 + 2(\epsilon - \epsilon')/m_r}$ where $m_r = m_A m_B/(m_A + m_B)$ is the reduced mass and m_A, m_B are masses of the colliding particles. We can write $\mathbf{u}' = u'(u)\mathbf{n}'$ and $\mathbf{v}_C = \mathbf{v} + u'(u)\mathbf{n}'$. From CM velocity conservation we have

$$m_A\mathbf{v}_A + m_B\mathbf{v}_B = m_A\mathbf{v}_C + m_B\mathbf{v} = (m_A + m_B\mathbf{v}) + m_A u'(u)\mathbf{n}' \tag{84}$$

and we also have $\mathbf{v}_A - \mathbf{v}_B = \mathbf{u}$. We solve $\mathbf{v}_A$, $\mathbf{v}_B$, $\mathbf{v}_C$ from these as

$$\mathbf{v}_A = \mathbf{v} + \frac{m_A}{m_A + m_B}u'(u)\mathbf{n}' + \frac{m_B}{m_A + m_B}\mathbf{u} \tag{85}$$

$$\mathbf{v}_B = \mathbf{v} + \frac{m_A}{m_A + m_B}u'(u)\mathbf{n}' - \frac{m_A}{m_A + m_B}\mathbf{u} \tag{86}$$

$$\mathbf{v}_C = \mathbf{v} + u'(u)\mathbf{n}' \tag{87}$$

$$u'(u) = \sqrt{u^2 + 2(\epsilon - \epsilon')/m_r}. \tag{88}$$

For one kind of gas ($m_A = m_B = m$) without internal states ($\varepsilon(A) = \varepsilon(B) = \varepsilon(C) = \varepsilon(D) = 0$) these equations reduce to

$$\mathbf{v}_A = \mathbf{v} + (u\mathbf{n}' + \mathbf{u})/\mathbf{2} \tag{89}$$

$$\mathbf{v}_B = \mathbf{v} + (u\mathbf{n}' - \mathbf{u})/\mathbf{2} \tag{90}$$

$$\mathbf{v}_C = \mathbf{v} + u\mathbf{n}'. \tag{91}$$

Again for one kind of gas ($m_A = m_B = m$ and $m_r = m/2$) with internal states (Eqs. 86–88) reduce to

$$\mathbf{v}_A = \mathbf{v} + [u'(u)\mathbf{n}' + \mathbf{u}]/2 \tag{92}$$

$$\mathbf{v}_B = \mathbf{v} + [u'(u)\mathbf{n}' - \mathbf{u}]/2 \tag{93}$$

$$\mathbf{v}_C = \mathbf{v} + u'(u)\mathbf{n}' \tag{94}$$

$$u'(u) = \sqrt{u^2 + 4(\epsilon - \epsilon')/m}. \tag{95}$$

For a mixture of gases without internal states Eqs. 85–88 reduce to

$$\mathbf{v}_A = \mathbf{v} + \frac{m_A}{m_A + m_B}u\mathbf{n}' + \frac{m_B}{m_A + m_B}\mathbf{u}, \tag{96}$$

$$\mathbf{v}_B = \mathbf{v} + \frac{m_A}{m_A + m_B}u\mathbf{n}' - \frac{m_A}{m_A + m_B} \tag{97}$$

$$\mathbf{v}_C = \mathbf{v} + u\mathbf{n}'. \tag{98}$$

And for a mixture of gases with internal states Eqs. 85–88 are the formulae.

3.2 One species of gas molecules without internal degrees of freedom

The state of particles are defined by three components of the velocity vector $\mathbf{v}$ (we use bold letters for vectors throughout this paper). Bird's original algorithm to keep track of time in the simulation was the 'time counter method'. Later Bird introduced 'No time counter method' (NTC) and declared time counter method 'obsolete' in his book [1]. Time counter method is more difficult (if not impossible) to formulate in the direct simulation formalism given in this paper, and since NTC is the algorithm currently used we will derive NTC algorithms only in this paper.

Here, the state index μ refer the velocity vectors and the integration over μ stands for three integrations over components of velocities. The NTC kernel $S(\mathbf{v}_A, \mathbf{v}_B; \mathbf{v}_C, \mathbf{v}) = S_1 + S_2$ is given by

$$S_1 = \frac{2}{R}\delta(\mathbf{H} - \mathbf{H}')\delta\left(u^2 - (u')^2\right)\sigma(\mathbf{n}, \mathbf{n}') \tag{99}$$

$$S_2 = \left(1 - \frac{u\Sigma}{R}\right)\delta(\mathbf{v}_C - \mathbf{v}_A)\delta(\mathbf{v} - \mathbf{v}_B). \tag{100}$$

Here $\sigma(\mathbf{n}, \mathbf{n}')$ is the differential cross-section and Σ is the total cross-section which is given by

$$\Sigma = \int \sigma(\mathbf{n}, \mathbf{n}')\mathrm{d}\mathbf{n}', \tag{101}$$

where $\mathrm{d}\mathbf{n}'$ is the solid angle in the direction of $\mathbf{n}'$. The $\sigma(\mathbf{n}, \mathbf{n}')$ depends on the angle θ between $\mathbf{n}$ and $\mathbf{n}'$ ($\mathbf{n}' \cdot \mathbf{n} = \cos\theta$). Hence $\sigma(\mathbf{n}, \mathbf{n}') = \sigma(\mathbf{n}', \mathbf{n})$ and the kernel is obviously symmetric. The term $\delta(u^2 - (u')^2) = \delta(u - u')/2u$ represents energy conservation and $\delta(\mathbf{H} - \mathbf{H}')$ represents conservation of center of mass (CM) velocity which is the same thing as the conservation of momentum. The kernel satisfies the normalization condition

$$\int S(\mathbf{v}_A, \mathbf{v}_B; \mathbf{v}_C, \mathbf{v})\mathrm{d}^3\mathbf{v}_C\mathrm{d}^3\mathbf{v} = \int S(\mathbf{v}_A, \mathbf{v}_B; \mathbf{v}_C, \mathbf{v})\mathrm{d}^3\mathbf{H}'\mathrm{d}^3\mathbf{u}' = 1. \tag{102}$$

Here the integral is taken in the CM coordinates. The Jacobian of the CM transformation is unity and $\mathrm{d}^3\mathbf{u}' = (u')^2\mathrm{d}u'\mathrm{d}\mathbf{n}'$.

The S_2 part of the kernel directly transfers initial velocities to the final velocities with a probability $(1 - u\Sigma/R)$ and hence causes a null collision. A null collision is a collision that particles do not change their states. The probability of making a real collision is

$$\int S_1(\mathbf{v}_A, \mathbf{v}_B; \mathbf{v}_C, \mathbf{v})\mathrm{d}^3\mathbf{v}_C\mathrm{d}^3\mathbf{v} = \frac{u\Sigma}{R} \tag{103}$$

where integral is calculated in the CM coordinates.

Inserting $S(\mathbf{v}_A, \mathbf{v}_B; \mathbf{v}_C, \mathbf{v})$ in Eq. 31 we obtain

$$\frac{\partial f(\mathbf{v})}{\partial \tau} = \int [f,f] S_1(\mathbf{v}_A, \mathbf{v}_B; \mathbf{v}_C, \mathbf{v}) \mathrm{d}^3\mathbf{v}_A \mathrm{d}^3\mathbf{v}_B \mathrm{d}^3\mathbf{v}_C. \tag{104}$$

where

$$[f,f] = f(\mathbf{v}_A) f(\mathbf{v}_B) - f(\mathbf{v}_C) f(\mathbf{v}). \tag{105}$$

The S_2 part of the kernel gives zero contribution in the collision integral

$$\int [f,f] \delta(\mathbf{v}_C - \mathbf{v}_A) \delta(\mathbf{v} - \mathbf{v}_B) \mathrm{d}^3\mathbf{v}_A \mathrm{d}^3\mathbf{v}_B \mathrm{d}^3\mathbf{v}_C = 0. \tag{106}$$

We evaluate the integral in Eq. 104 in the CM coordinates. We write $\mathrm{d}^3\mathbf{v}_A \mathrm{d}^3\mathbf{v}_B = \mathrm{d}^3\mathbf{H} \mathrm{d}^3\mathbf{u}$ and $\mathrm{d}^3\mathbf{v}_C = \mathrm{d}^3\mathbf{u}' = (u')^2 \mathrm{d}u' \mathrm{d}\mathbf{n}'$. When we do the integral we obtain

$$\frac{\partial f(\mathbf{v})}{\partial \tau} = \frac{1}{R} \int [f,f] u\sigma(\mathbf{n}, \mathbf{n}') \mathrm{d}^3\mathbf{u} \mathrm{d}\mathbf{n}', \tag{107}$$

where $\mathbf{v}_A$, $\mathbf{v}_B$, $\mathbf{v}_C$ are expressed in terms of the variables $\mathbf{v}, \mathbf{u}, \mathbf{n}'$ in Eqs. 89–91.

The Eq. 107 is essentially the Boltzmann equation with the difference that the Boltzmann equation is written for density in physical space. To obtain the Boltzmann equation we write this equation for $F(\mathbf{v}) = (N/V) f(\mathbf{v})$ where V is the volume of the gas. Then we obtain

$$\frac{\partial F(\mathbf{v})}{\partial \tau} = \frac{1}{R} \left(\frac{V}{N}\right) \int [F(\mathbf{v}_A) F(\mathbf{v}_B) - F(\mathbf{v}_C) F(\mathbf{v})] \times u\sigma(\mathbf{n}, \mathbf{n}') \mathrm{d}^3\mathbf{u} \mathrm{d}\mathbf{n}'. \tag{108}$$

Now, if we change to the variable $t = \tau V/RN = 2nV/RN^2$ we obtain the Boltzmann equation for a homogenous gas

$$\frac{\partial F(\mathbf{v})}{\partial t} = \int [F(\mathbf{v}_A) F(\mathbf{v}_B) - F(\mathbf{v}_C) F(\mathbf{v})] u\sigma(\mathbf{n}, \mathbf{n}') \mathrm{d}^3\mathbf{u} \mathrm{d}\mathbf{n}'. \tag{109}$$

Here, t must be interpreted as the physical time and $t = 2nV/RN^2$ formula connects the physical time t and number of collision attempts n.

Let us state the algorithm for a homogenous gas. We choose a number R big enough such that for only very few (say less than one in thousand) pairs $u\Sigma/R$ will exceed unity. We make $n = RN^2 t/2V$ collision attempts to reach the desired time. For each pair we take a random number r distributed evenly between 0 and 1, and we allow the collision to happen if $r < u\Sigma/R$. If the collision is allowed, we choose the direction of scattering $\mathbf{n}'$ according to the probability density $\sigma(\mathbf{n}, \mathbf{n}')/\Sigma$ and a few more random numbers are used for that. Then we calculate and store final velocities for the colliding pairs and pick another pair. We keep taking and colliding pairs until we reach the desired time.

Suppose the formula $n = RN^2 t/2V$ yields 234.783 collisions. How do you make 0.783 collisions? The way to do this in practice is to make 234 collisions first. Then throw a random number r and if $r < 0.783$ then go on to make a collision attempt. This can be justified from the formula

$$f(\mu; n+1) = -f(\mu; n) + \frac{2}{N} \int [f,f] T(\mu_A, \mu_B; \mu_C, \mu) \mathrm{d}\mu_A \mathrm{d}\mu_B \mathrm{d}\mu_C. \tag{110}$$

After making n collision attempts with the NTC kernel $S(\mathbf{v}_A, \mathbf{v}_B; \mathbf{v}_C, \mathbf{v})$ we can change the kernel to

$$P(\mathbf{v}_A, \mathbf{v}_B; \mathbf{v}_C, \mathbf{v}) = qS(\mathbf{v}_A, \mathbf{v}_B; \mathbf{v}_C, \mathbf{v}) + (1-q)\delta(\mathbf{v}_C - \mathbf{v}_A)\delta(\mathbf{v} - \mathbf{v}_B). \tag{111}$$

This kernel makes a NTC collision attempt with a probability q (which was 0.783 in the above example) and a null collision happens with the probability $1 - q$. We use this kernel for the $(n + 1)$th collision attempt (it is permissible to change the kernel), and this causes another $\Delta\tau = 2q/N$ collision time and $\Delta t = q(2V/RN^2)$ real time increase.

3.3 Mixture of gases without internal degrees of freedom

The state of particles are defined by three components of the velocity vector $\mathbf{v}$ and one index denoting the species of molecules for which we will use p, q, r, s characters. We have M species of gas molecules without internal states in the mixture, and there are N_p number of molecules of the pth species. The mass of pth species of molecules is m_p. The probability density $f(\mu) = f(\mathbf{v},p)$ will be written as $f^p(\mathbf{v})$.

Particles with states $\mu_A = (\mathbf{v}_A,s)$, and $\mu_B = (\mathbf{v}_B,r)$ enter the collision and particles with states $\mu_C = (\mathbf{v}_C,q)$ and $\mu_D = (\mathbf{v},p)$ exits the collision. The integration over μ such as $\int f^p(\mathbf{v})\mathrm{d}\mu$ stands for three integrations over $\mathbf{v}$ and summation over p. The center of mass (CM) coordinates are defined in Eqs. 78–80.

The NTC kernel $G^{rs}_{pq}(\mathbf{v}_A, \mathbf{v}_B; \mathbf{v}_C, \mathbf{v}) = G_1 + G_2$ is given by

$$G_1 = \frac{2}{R} \delta(\mathbf{H} - \mathbf{H}') \delta\left(u^2 - (u')^2\right) \sigma_{pq}(\mathbf{n}, \mathbf{n}') \delta_{pr} \delta_{qs}, \tag{112}$$

$$G_2 = \left(1 - \frac{u\Sigma_{pq}}{R}\right) \delta(\mathbf{v}_C - \mathbf{v}_A) \delta(\mathbf{v} - \mathbf{v}_B) \delta_{pr} \delta_{qs}. \tag{113}$$

Here, $\sigma_{pq}(\mathbf{n}, \mathbf{n}')$ is the differential cross-section between gases of the pth and qth kind, and Σ_{pq} is the total cross-section which is given by

$$\Sigma_{pq} = \int \sigma_{pq}(\mathbf{n}, \mathbf{n}') \mathrm{d}\mathbf{n}', \tag{114}$$

where $\mathrm{d}\mathbf{n}'$ is the solid angle in the direction of $\mathbf{n}'$. The $\delta_{pr}\delta_{qs}$ term in the kernel insures that particles do not loose

their identities during the collisions. Again $\sigma_{pq}(\mathbf{n},\mathbf{n}') = \sigma_{rs}(\mathbf{n},\mathbf{n}')$ due to the $\delta_{pr}\delta_{qs}$ term, and we also have the symmetry $\sigma_{pq}(\mathbf{n},\mathbf{n}') = \sigma_{qp}(\mathbf{n}',\mathbf{n})$. The kernel is obviously symmetric. The term $\delta(u^2-(u')^2)$ and $\delta(\mathbf{H}-\mathbf{H}')$ have the same meanings as before, and the kernel satisfies the normalization condition

$$\sum_{p=1}^{M}\sum_{q=1}^{M}\int G_{pq}^{rs}(\mathbf{v}_A,\mathbf{v}_B;\mathbf{v}_C,\mathbf{v})\mathrm{d}^3\mathbf{v}_C\mathrm{d}^3\mathbf{v} = 1. \tag{115}$$

Again G_2 part of the kernel directly transfer initial velocities to the final velocities with a probability $1-(u\Sigma_{rs})/R$, and hence causes a null collision. The probability of making a real collision is

$$\sum_{p=1}^{M}\sum_{q=1}^{M}\int (G_1)_{pq}^{rs}(\mathbf{v}_A,\mathbf{v}_B;\mathbf{v}_C,\mathbf{v})\mathrm{d}^3\mathbf{v}_C\mathrm{d}^3\mathbf{v} = \frac{u\Sigma_{rs}}{R}, \tag{116}$$

where integral is calculated in the CM coordinates.

Inserting $G_{pq}^{rs}(\mathbf{v}_A,\mathbf{v}_B;\mathbf{v}_C,\mathbf{v})$ in Eq. 31 and doing the summations over *r*,*s* and doing the integrals in the CM coordinates we obtain

$$\frac{\partial f^p(\mathbf{v})}{\partial\tau} = \sum_{q=1}^{M}\int G_{pq}^{pq}(\mathbf{v}_A,\mathbf{v}_B;\mathbf{v}_C,\mathbf{v})[f^q,f^p]\mathrm{d}^3\mathbf{v}_A\mathrm{d}^3\mathbf{v}_B\mathrm{d}^3\mathbf{v}_C, \tag{117}$$

$$= \frac{1}{R}\sum_{q=1}^{M}\int [f^q,f^p]u\sigma_{pq}(\mathbf{n},\mathbf{n}')\mathrm{d}^3\mathbf{n}\mathrm{d}\mathbf{n}', \tag{118}$$

where

$$[f^q,f^p] = f^q(\mathbf{v}_A)f^p(\mathbf{v}_B) - f^q(\mathbf{v}_C)f^p(\mathbf{v}). \tag{119}$$

Again we write this equation for $F^p(\mathbf{v}) = (N/V)f^p(\mathbf{v})$ and take $t = 2nV/RN^2$ to obtain Boltzmann equation for a mixture of homogenous gases without internal states

$$\frac{\partial F^p(\mathbf{v})}{\partial t} = \sum_{q=1}^{M}\int [F^q(\mathbf{v}_A)F^p(\mathbf{v}_B) - F^q(\mathbf{v}_C)F^p(\mathbf{v})] \times u\sigma_{pq}(\mathbf{n},\mathbf{n}')\mathrm{d}^3\mathbf{u}\mathrm{d}\mathbf{n}'. \tag{120}$$

Here $\mathbf{v}_A,\mathbf{v}_B,\mathbf{v}_C$ are expressed in terms of the variables **v, u,** $\mathbf{n}'$ in Eqs. 96–98.

The algorithm is the same. We take $n = RN^2t/2V$ pairs and allow each collision with a probability $(u\Sigma_{rs})/R$. If the collision is allowed we choose the scattering angle according to the $\sigma_{rs}(\mathbf{n},\mathbf{n}')/\Sigma_{rs}$ probability distribution.

Note that the normalization of $f^p(\mathbf{v})$is given by

$$\sum_{p=1}^{M}\int f^p(\mathbf{v})\mathrm{d}^3\mathbf{v} = 1. \tag{121}$$

The integral $\int f^p(\mathbf{v})\mathrm{d}^3\mathbf{v}$ is conserved during the simulation. From Eq. 117 its rate of change is

$$\frac{\mathrm{d}}{\mathrm{d}\tau}\int f^p(\mathbf{v})\mathrm{d}^3\mathbf{v} = \int\frac{\partial f^p(\mathbf{v})}{\partial\tau}\mathrm{d}^3\mathbf{v} = \sum_{q=1}^{M}\int G_{pq}^{pq}(\mathbf{v}_A,\mathbf{v}_B;\mathbf{v}_C,\mathbf{v}) \times [f^q(\mathbf{v}_A)f^p(\mathbf{v}_B) - f^q(\mathbf{v}_C)f^p(\mathbf{v})] \times \mathrm{d}^3\mathbf{v}_A\mathrm{d}^3\mathbf{v}_B\mathrm{d}^3\mathbf{v}_C\mathrm{d}^3\mathbf{v}. \tag{122}$$

From normalization of probabilities in Eqs. 3, 115 we have

$$\int G_{pq}^{pq}(\mathbf{v}_A,\mathbf{v}_B;\mathbf{v}_C,\mathbf{v})\mathrm{d}^3\mathbf{v}_C\mathrm{d}^3\mathbf{v} = 1 \tag{123}$$

$$\int G_{pq}^{pq}(\mathbf{v}_A,\mathbf{v}_B;\mathbf{v}_C,\mathbf{v})\mathrm{d}^3\mathbf{v}_A\mathrm{d}^3\mathbf{v}_B = 1. \tag{124}$$

Using these relations the integral on the right side of Eq. 122 can be written as

$$\frac{\mathrm{d}}{\mathrm{d}\tau}\int f^p(\mathbf{v})\mathrm{d}^3\mathbf{v} = \sum_{q=1}^{M}\int f^q(\mathbf{v}_A)f^p(\mathbf{v}_B)\mathrm{d}^3\mathbf{v}_A\mathrm{d}^3\mathbf{v}_B - \sum_{q=1}^{M}\int f^q(\mathbf{v}_C)f^p(\mathbf{v})\mathrm{d}^3\mathbf{v}_C\mathrm{d}^3\mathbf{v}. \tag{125}$$

These two terms are equal and they cancel each other yielding constancy of $\int f^p(\mathbf{v})\mathrm{d}^3\mathbf{v}$.

The number of molecules of the *p*th species is

$$N_p = N\int f^p(\mathbf{v})\mathrm{d}^3\mathbf{v}, \tag{126}$$

and it remains constant as it should. Hence the $F^p(\mathbf{v})$ is normalized as

$$\int F^p(\mathbf{v})\mathrm{d}^3\mathbf{v}\mathrm{d}^3\mathbf{x} = N_p, \tag{127}$$

where **x** is position of the molecule.

3.4 One species of gas molecules with internal degrees of freedom

For a homogeneous gas with internal states the μ stands for velocity **v** and a discrete index (for which we use α, β, *i*, *j*) defining the internal quantum state of the molecule. The mass of the molecules is *m*. Particles with states $\mu_A = (\mathbf{v}_A, \beta)$ and $\mu_B = (\mathbf{v}_B, \alpha)$ enter the collision and particles with states $\mu_C = (\mathbf{v}_C, j)$ and $\mu_D = (\mathbf{v}, i)$ exits the collision. The integral over μ stands for integration over **v** and summation over the internal state index. The internal energy of molecule in the state γ is E_γ and $\varepsilon = E_\alpha + E_\beta$ and $\varepsilon' = E_i + E_j$. The center of mass (CM) coordinates are defined in Eqs. 80 and 81.

Let us define the no time counter (NTC) kernel $K_{ij}^{\alpha\beta}(\mathbf{v}_A,\mathbf{v}_B;\mathbf{v}_C,\mathbf{v}) = K_1 + K_2$ where

$$K_1 = \frac{1}{R}\delta(\mathbf{H}-\mathbf{H}')\delta\left[\frac{2}{m_r}\epsilon + u^2 - \frac{2}{m_r}\epsilon' - (u')^2\right] \times \frac{2u}{u'}\sigma_{ij}^{\alpha\beta}(\mathbf{n},\mathbf{n}'), \quad (128)$$

and

$$K_2 = \left(1 - \frac{1}{R}\sum_i\sum_j u\Sigma_{ij}^{\alpha\beta}\right)\delta(\mathbf{v}_C - \mathbf{v}_A)\delta(\mathbf{v}-\mathbf{v}_B)\delta_{i\alpha}\delta_{j\beta}. \quad (129)$$

Here $m_r = m/2$ is the reduced mass where m is the mass of the molecules and R is a chosen parameter. The $\sigma_{ij}^{\alpha\beta}(\mathbf{n},\mathbf{n}')$ is differential and the $\Sigma_{ij}^{\alpha\beta}$ is the total cross-section into the internal states i, j

$$\Sigma_{ij}^{\alpha\beta} = \int \sigma_{ij}^{\alpha\beta}(\mathbf{n},\mathbf{n}')\mathrm{d}\mathbf{n}', \quad (130)$$

where $\mathrm{d}\mathbf{n}'$ is the solid angle in the direction of $\mathbf{n}'$. This kernel is symmetric due to the reciprocity relation of the inelastic scattering cross-sections [16]

$$u^2\sigma_{ij}^{\alpha\beta}(\mathbf{n},\mathbf{n}') = (u')^2\sigma_{\alpha\beta}^{ij}(\mathbf{n}',\mathbf{n}), \quad (131)$$

because $(u/u')\sigma_{ij}^{\alpha\beta} = (u'/u)\sigma_{\alpha\beta}^{ij}$.

The K_2 part of $K_{ij}^{\alpha\beta}(\mathbf{v}_A,\mathbf{v}_B;\mathbf{v}_C,\mathbf{v})$ directly transfers initial state to the final state and causes a null collision. The probability of making a real collision into the states (i, j) is

$$P_{ij} = \int K_1 \mathrm{d}\mathbf{v}_C\mathrm{d}\mathbf{v} = \frac{u\Sigma_{ij}^{\alpha\beta}}{R}. \quad (132)$$

Therefore total probability of making a real collision is $(\sum_i\sum_j u\Sigma_{ij}^{\alpha\beta})/R$.

Inserting the $K_{ij}^{\alpha\beta}(\mathbf{v}_A,\mathbf{v}_B;\mathbf{v}_C,\mathbf{v})$ into the Eq. 31 and doing the integrals in the CM coordinates we obtain

$$\frac{\partial f_i(\mathbf{v})}{\partial\tau} = \frac{1}{R}\sum_\alpha\sum_\beta\sum_j\int\left[f_\beta(\mathbf{v}_A)f_\alpha(\mathbf{v}_B) - f_j(\mathbf{v}_C)f_i(\mathbf{v})\right] \times u\sigma_{ij}^{\alpha\beta}(\mathbf{n},\mathbf{n}')\mathrm{d}^3\mathbf{u}\mathrm{d}\mathbf{n}'. \quad (133)$$

Here the K_2 part does not contribute to the collision integral as before.

Again defining time as $t = \tau V/RN = 2nV/RN^2$ and defining the new functions $F_i(\mathbf{v}) = (N/V)f_i(\mathbf{v})$ this is expressed as

$$\frac{\partial F_i}{\partial t} = \sum_\alpha\sum_\beta\sum_j\int\left[F_\beta(\mathbf{v}_A)F_\alpha(\mathbf{v}_B) - F_j(\mathbf{v}_C)F_i(\mathbf{v})\right] \times u\sigma_{ij}^{\alpha\beta}(\mathbf{n},\mathbf{n}')\mathrm{d}^3\mathbf{u}\mathrm{d}\mathbf{n}', \quad (134)$$

where $\mathbf{v}_A$, $\mathbf{v}_B$, $\mathbf{v}_C$ are expressed in terms of the variables $\mathbf{v},\mathbf{u},\mathbf{n}'$ in Eqs. 92–95. These equations are the Wang Chang–Uhlenbeck equations for a gas with internal degrees of freedom. Here the states are assumed nondegenerate for simplicity. Generalization to degenerate states is also very straightforward.

Again we choose a number R big enough such that for only very few (say less than one in thousand) pairs $(\sum_i\sum_j u\Sigma_{ij}^{\alpha\beta})/R$ will exceed unity. We chose $n = RN^2t/2V$ random pairs. For each pair we take a random number r and we allow the collision to happen if $r < (\sum_i\sum_j u\Sigma_{ij}^{\alpha\beta})/R$. If collision is allowed we choose the final state (i, j) with the probability $\Sigma_{ij}^{\alpha\beta}/(\sum_i\sum_j\Sigma_{ij}^{\alpha\beta})$ and another random number is used to choose the final state. Finally, we choose the direction of scattering $\mathbf{n}'$ according to the probability density $\sigma_{ij}^{\alpha\beta}(\mathbf{n},\mathbf{n}')/\Sigma_{ij}^{\alpha\beta}$ and a few more random numbers are used for that. Then we calculate and store final velocities and state indices for the colliding pair and go on to choose next pair.

3.5 Mixture of gases with internal degrees of freedom

This case is a combination of previous two cases and it is very straightforward but unfortunately there are too many indices. The state of particles are defined by three components of the velocity vector $\mathbf{v}$ and one index denoting species of the molecules for which we use p, q, r, s and one internal state index for which we use i, j, α, β. We have M species of molecules with internal states in the mixture, and there are N_p number of molecules of the pth species. The internal energy of ith internal state of pth species of molecules is E_i^p. The probability density $f(\mu) = f(\mathbf{v}, i, p)$ will be written as $f_i^p(\mathbf{v})$.

Particles with states $\mu_A = (\mathbf{v}_A, \beta, s)$, and $\mu_B = (\mathbf{v}_B, \alpha, r)$ enter the collision and particles with states $\mu_C = (\mathbf{v}_C, j, q)$ and $\mu_D = (\mathbf{v}, i, p)$ exits the collision. We also define $\varepsilon = E_\beta^s + E_\alpha^r$ and $\varepsilon' = E_j^q + E_i^p$. The integration over μ such as $\int f_i^p(\mathbf{v})\mathrm{d}\mu$ stands for three integrations over $\mathbf{v}$ and summations over i and p. The center of mass (CM) coordinates are defined in Eqs. 78–80.

The NTC kernel is $Q_{ij,pq}^{\alpha\beta,rs}(\mathbf{v}_A,\mathbf{v}_B;\mathbf{v}_C,\mathbf{v}) = Q_1 + Q_2$ where Q_1 and Q_2 are defined as

$$Q_1 = \frac{1}{R}\delta(\mathbf{H}-\mathbf{H}')\delta\left[\frac{2}{m_r}\epsilon + u^2 - \frac{2}{m_r}\epsilon' - (u')^2\right] \times \frac{2u}{u'}\sigma_{ij,pq}^{\alpha\beta,pq}(\mathbf{n},\mathbf{n}')\delta_{pr}\delta_{qs} \quad (135)$$

and

$$Q_2 = \left(1 - \frac{1}{R}\sum_i\sum_j u\Sigma_{ij,pq}^{\alpha\beta,pq}\right)\delta(\mathbf{v}_C - \mathbf{v}_A)\delta(\mathbf{v} - \mathbf{v}_B)\delta_{i\alpha}\delta_{j\beta}\delta_{pr}\delta_{qs}. \quad (136)$$

The delta functions $\delta_{pr}\delta_{qs}$ insures that the molecules do no change identities during the collision. Here, $m_r = m_Am_B/(m_A + m_B)$ is the reduced mass, R is a chosen parameter. The $\sigma_{ij,pq}^{\alpha\beta,pq}(\mathbf{n},\mathbf{n}')$ is the differential cross-section between

pth species in the state α and qth species in the state β, and $\Sigma_{ij,pq}^{\alpha\beta,pq}$ is the total cross-section into the channel (i, j)

$$\Sigma_{ij,pq}^{\alpha\beta,pq} = \int \sigma_{ij,pq}^{\alpha\beta,pq}(\mathbf{n},\mathbf{n}')\mathrm{d}\mathbf{n}' \tag{137}$$

where $\mathrm{d}\mathbf{n}'$ is the solid angle in the direction of $\mathbf{n}'$. The $Q_{ij,pq}^{\alpha\beta,rs}(\mathbf{v}_A,\mathbf{v}_B;\mathbf{v}_C,\mathbf{v})$ is also symmetric due to Eq. 131. The Q_2 directly transfers initial states to the final states and causes a null collision. The probability of making a real collision into the states (i, j) is

$$P_{ij} = \int Q_1 \mathrm{d}\mathbf{v}_C \mathrm{d}\mathbf{v} = \frac{u\Sigma_{ij,pq}^{\alpha\beta,pq}}{R}. \tag{138}$$

Therefore total probability of making a real collision is $(\sum_i \sum_j u\Sigma_{ij,pq}^{\alpha\beta,pq})/R$.

Inserting the $Q_{ij,pq}^{\alpha}\beta, rs(\mathbf{v}_A, \mathbf{v}_B; \mathbf{v}_C, \mathbf{v})$ into the Eq. 31 and doing the integrals in the CM coordinates we obtain

$$\frac{\partial f_i^p(\mathbf{v})}{\partial\tau} = \sum_{q=1}^{M}\sum_{\alpha}\sum_{\beta}\sum_{j}\int [f^q,f^p]_{ij}^{\alpha\beta} \times Q_{ij,pq}^{\alpha\beta,pq}(\mathbf{v}_A,\mathbf{v}_B;\mathbf{v}_C,\mathbf{v})\mathrm{d}^3\mathbf{v}_A\mathrm{d}^3\mathbf{v}_B\mathrm{d}^3\mathbf{v}_C, \tag{139}$$

where

$$[f^q,f^p]_{ij}^{\alpha\beta} = f_\beta^q(\mathbf{v}_A)f_\alpha^p(\mathbf{v}_B) - f_j^q(\mathbf{v}_C)f_i^p(\mathbf{v}). \tag{140}$$

After inserting $Q_{ij,pq}^{\alpha\beta,pq}$ we obtain

$$\frac{\partial f_i^p(\mathbf{v})}{\partial\tau} = \frac{1}{R}\sum_{q=1}^{M}\sum_{\alpha}\sum_{\beta}\sum_{j}\int [f^q,f^p]_{ij}^{\alpha\beta} u\sigma_{ij,pq}^{\alpha\beta,pq}(\mathbf{n},\mathbf{n}')\mathrm{d}^3\mathbf{u}\mathrm{d}\mathbf{n}'. \tag{141}$$

The Q_2 part does not contribute to the collision integral as before. Expressions of $\mathbf{v}_A$, $\mathbf{v}_B$, $\mathbf{v}_C$ in terms of $\mathbf{v}, \mathbf{u}, \mathbf{n}'$ are given in Eqs. 85–88.

Again defining time as $t = \tau V/RN = 2nV/RN^2$ and defining the new functions $F_i^p(\mathbf{v}) = (N/V)\ f_i^p(\mathbf{v})$ this is expressed as

$$\frac{\partial F_i^p(\mathbf{v})}{\partial t} = \sum_{q=1}^{M}\sum_{\alpha}\sum_{\beta}\sum_{j}\int \left(F_\beta^q(\mathbf{v}_A)F_\alpha^p(\mathbf{v}_B) - F_j^q(\mathbf{v}_C)F_i^p(\mathbf{v})\right) \times u\sigma_{ij,pq}^{\alpha\beta,pq}(\mathbf{n},\mathbf{n}')\mathrm{d}^3\mathbf{u}\mathrm{d}\mathbf{n}'. \tag{142}$$

These equations are the Wang Chang–Uhlenbeck equations for a mixture of gases with internal degrees of freedom. Here the states are assumed nondegenerate for simplicity again.

Again we choose a number R big enough such that for only very few (say less than one in thousand) pairs $(\sum_i \sum_j u\Sigma_{ij,pq}^{\alpha\beta,pq})/R$ will exceed unity. We chose $n = RN^2t/2V$ random pairs. For each pair we take a random number r, and we allow the collision to happen if $r < (\sum_i \sum_j u\Sigma_{ij,pq}^{\alpha\beta,pq})/R$. If collision is allowed we choose the final state (i, j) with the probability $\Sigma_{ij,pq}^{\alpha\beta,pq}/(\sum_i \sum_j \Sigma_{ij,pq}^{\alpha\beta,pq})$, and another random number is used to choose the final state. Finally we choose the direction of scattering $\mathbf{n}'$ according to the probability density $\sigma_{ij,pq}^{\alpha\beta,pq}(\mathbf{n},\mathbf{n}')/\Sigma_{ij,pq}^{\alpha\beta,pq}$, and a few more random numbers are used for that. Then we calculate and store final velocities and state indices for the colliding pair and go on to choose next pair.

Note that the normalization of $f_i^p(\mathbf{v})$is given by

$$\sum_p\sum_i\int f_i^p(\mathbf{v})\mathrm{d}^3\mathbf{v} = 1. \tag{143}$$

The expression $\sum_i \int f_i^p(\mathbf{v})\mathrm{d}^3\mathbf{v}$ is conserved during the simulation. From Eq. 139 its rate of change is

$$\frac{\mathrm{d}}{\mathrm{d}\tau}\sum_i\int f_i^p(\mathbf{v})\mathrm{d}^3\mathbf{v} = \sum_i\int\frac{\partial f_i^p(\mathbf{v})}{\partial\tau}\mathrm{d}^3\mathbf{v} = \sum_{q=1}^{M}\sum_{\alpha}\sum_{\beta}\sum_{i}\sum_{j}\int [f^q,f^p]_{ij}^{\alpha\beta} \times Q_{ij,pq}^{\alpha\beta,pq}(\mathbf{v}_A,\mathbf{v}_B;\mathbf{v}_C,\mathbf{v})\mathrm{d}^3\mathbf{v}_A\mathrm{d}^3\mathbf{v}_B\mathrm{d}^3\mathbf{v}_C\mathrm{d}^3\mathbf{v}. \tag{144}$$

From symmetry and normalization of the kernel given in Eqs. 1–3 we have

$$\sum_i\sum_j\int Q_{ij,pq}^{\alpha\beta,pq}(\mathbf{v}_A,\mathbf{v}_B;\mathbf{v}_C,\mathbf{v})\mathrm{d}^3\mathbf{v}_C\mathrm{d}^3\mathbf{v} = 1 \tag{145}$$

$$\sum_\alpha\sum_\beta\int Q_{ij,pq}^{\alpha\beta,pq}(\mathbf{v}_A,\mathbf{v}_B;\mathbf{v}_C,\mathbf{v})\mathrm{d}^3\mathbf{v}_A\mathrm{d}^3\mathbf{v}_B = 1. \tag{146}$$

Using this, we express Eq. 144 as

$$\frac{\mathrm{d}}{\mathrm{d}\tau}\sum_i\int f_i^p(\mathbf{v})\mathrm{d}^3\mathbf{v} = \sum_{q=1}^{M}\sum_{\alpha}\sum_{\beta}\int f_\beta^q(\mathbf{v}_A)f_\alpha^p(\mathbf{v}_B)\mathrm{d}^3\mathbf{v}_A\mathrm{d}^3\mathbf{v}_B - \sum_{q=1}^{M}\sum_{i}\sum_{j}\int f_j^q(\mathbf{v}_C)f_i^p(\mathbf{v})\mathrm{d}^3\mathbf{v}_C\mathrm{d}^3\mathbf{v}. \tag{147}$$

These two terms are equal and they cancel each other yielding constancy of $\sum_i f_i^p(\mathbf{v})\mathrm{d}^3\mathbf{v}$. The number of molecules of the pth kind is

$$N_p = N\sum_i\int f_i^p(\mathbf{v})\mathrm{d}^3\mathbf{v} \tag{148}$$

and as the above argument shows, it remains constant as it should. Hence the $F_i^p(\mathbf{v})$ is normalized as

$$\sum_i\int F_i^p(\mathbf{v})\mathrm{d}^3\mathbf{v}\mathrm{d}^3\mathbf{x} = N_p, \tag{149}$$

where $\mathbf{x}$ is position of the molecule.

4 Direct simulation for an inhomogeneous gas

In this section we study NTC algorithm of DSMC method for inhomogeneous gas. We will not actually derive Bird's algorithm but we will define a similar algorithm to simulate inhomogeneous gas. We will show that single particle probability distribution of our algorithm satisfies the Boltzmann equation for an inhomogeneous gas. Then we will argue that both algorithms give the same results in the limit $N\to\infty$.

We divide the physical space into cells and the kth cell has the volume V_k. Now let us define the functions

$$\Delta_k(\mathbf{x}) = \begin{cases} 1 & \mathbf{x} \in V_k \\ 0 & \mathbf{x} \notin V_k \end{cases}. \tag{150}$$

We will also need the function

$$\Gamma(\mathbf{x},\mathbf{x}') = \sum_k \frac{\Delta_k(\mathbf{x})\Delta_k(\mathbf{x}')}{V_k}. \tag{151}$$

This function is zero when $\mathbf{x}$ and $\mathbf{x}'$ are not in the same cell and $1/V_k$ when they are in the same cell. Its integral over $\mathbf{x}$ or $\mathbf{x}'$ is unity

$$\int \Gamma(\mathbf{x},\mathbf{x}')\mathrm{d}^3\mathbf{x}' = \int \Gamma(\mathbf{x},\mathbf{x}')\mathrm{d}^3\mathbf{x} = 1. \tag{152}$$

At the end of this section we will take the limit $V_k\to 0$. In this limit $\Gamma(\mathbf{x},\mathbf{x}') = 0$ for $\mathbf{x} \neq \mathbf{x}'$ and $\Gamma(\mathbf{x},\mathbf{x}') = \infty$ for $\mathbf{x} = \mathbf{x}'$, and Eq. 152 is still satisfied. These are properties of the Dirac delta function and we have the limit

$$\lim_{V_k\to 0} \Gamma(\mathbf{x},\mathbf{x}') = \delta(\mathbf{x}-\mathbf{x}'). \tag{153}$$

Now we can start the discussion. We will treat the simplest case for clarity. We develop our arguments for one kind of gas without internal degrees of freedom. The generalization to the other cases is very straightforward and will be summarized at the end of the section.

The state index μ represents position of the particle $\mathbf{x}$ and the velocity $\mathbf{v}$. The collision kernel is $Z = Z_1 + Z_2$ where Z_1 and Z_2 are

$$Z_1(\mathbf{x}_A,\mathbf{v}_A,\mathbf{x}_B,\mathbf{v}_B;\mathbf{x}_C,\mathbf{v}_C,\mathbf{x}_D,\mathbf{v}_D) = S(\mathbf{v}_A,\mathbf{v}_B;\mathbf{v}_C\mathbf{v}_D)\Omega\Gamma(\mathbf{x}_A,\mathbf{x}_B) \times \delta(\mathbf{x}_C-\mathbf{x}_A)\delta(\mathbf{x}_D-\mathbf{x}_B), \tag{154}$$

and

$$Z_2(\mathbf{x}_A,\mathbf{v}_A,\mathbf{x}_B,\mathbf{v}_B;\mathbf{x}_C,\mathbf{v}_C,\mathbf{x}_D,\mathbf{v}_D) = (1-\Omega\Gamma(\mathbf{x}_A,\mathbf{x}_B)) \times \delta(\mathbf{x}_C-\mathbf{x}_A)\delta(\mathbf{x}_D-\mathbf{x}_B)\delta(\mathbf{v}_C-\mathbf{v}_A)\delta(\mathbf{v}_D-\mathbf{v}_B). \tag{155}$$

Here

$$\Omega = \left(\sum_k \frac{1}{V_k}\right)^{-1}, \tag{156}$$

is a constant chosen to insure that probability of making a collision in any cell is less than unity. The $S(\mathbf{v}_A,\mathbf{v}_B;\mathbf{v}_C,\mathbf{v}_D)$ is given in Eqs. 99 and 100. The Z_2 does not change states of the of the particles and the pair will not be allowed to make a collision attempt with a probability $(1-\Omega\Gamma(\mathbf{x}_A,\mathbf{x}_B))$. The probability of a collision attempt is $\Omega\Gamma(\mathbf{x}_A,\mathbf{x}_B)$, and in a real collision positions of particles do not change because of the $\delta(\mathbf{x}_C-\mathbf{x}_A)\,\delta(\mathbf{x}_D-\mathbf{x}_B)$ term in the Z. The $Z(\mathbf{x}_A,\mathbf{v}_A,\mathbf{x}_B,\mathbf{v}_B;\mathbf{x}_C,\mathbf{v}_C,\mathbf{x}_D,\mathbf{v}_D)$ is symmetric and satisfies the normalization condition

$$\int Z(\mathbf{x}_A,\mathbf{v}_A,\mathbf{x}_B,\mathbf{v}_B;\mathbf{x}_C,\mathbf{v}_C,\mathbf{x}_D,\mathbf{v}_D)\mathrm{d}^3\mathbf{v}_A\mathrm{d}^3\mathbf{v}_B\mathrm{d}^3\mathbf{x}_A\mathrm{d}^3\mathbf{x}_B = 1, \tag{157}$$

$$\int Z(\mathbf{x}_A,\mathbf{v}_A,\mathbf{x}_B,\mathbf{v}_B;\mathbf{x}_C,\mathbf{v}_C,\mathbf{x}_D,\mathbf{v}_D)\mathrm{d}^3\mathbf{v}_C\mathrm{d}^3\mathbf{v}_D\mathrm{d}^3\mathbf{x}_C\mathrm{d}^3\mathbf{x}_D = 1. \tag{158}$$

The $\Omega\Gamma(\mathbf{x}_A,\mathbf{x}_B)$ vanishes unless $\mathbf{x}_A$ and $\mathbf{x}_B$ are in the same cell and $\Omega\Gamma(\mathbf{x}_A,\mathbf{x}_B) = \Omega/V_k$ when $\mathbf{x}_A$ and $\mathbf{x}_B$ are in the cell V_k. The probability of having both particles in the cell V_k is $(N_k/N)^2$ where N_k is the number of particles in the cell V_k during the collisions part of the simulation. Therefore the probability of a pair making a collision attempt in the kth cell is $p_k = (\Omega/V_k)(N_k/N)^2$. The $1/V_k$ term looks awkward in this probability but it is absolutely necessary as the following argument shows. Suppose the physical density is uniform and therefore $N_k/N = V_k/V$ where V is the total volume. When density is uniform we expect that the probability of having a collision in V_k is proportional to V_k. When $N_k/N = V_k/V$ is inserted in p_k we find $p_k = \Omega V_k/V^2$ which is proportional to V_k as expected.

Now we insert the kernel Z in the Eq. 31 to obtain

$$\frac{\partial f(\mathbf{x},\mathbf{v},\tau)}{\partial\tau} = \int [f,f]Z(\mathbf{x}_A,\mathbf{v}_A,\mathbf{x}_B,\mathbf{v}_B;\mathbf{x}_C,\mathbf{v}_C,\mathbf{x}) \times \mathrm{d}^3\mathbf{v}_A\mathrm{d}^3\mathbf{v}_B\mathrm{d}^3\mathbf{v}_C\mathrm{d}^3\mathbf{x}_A\mathrm{d}^3\mathbf{x}_B\mathrm{d}^3\mathbf{x}_C \tag{159}$$

where $[f,f]$ is

$$[f,f] = f(\mathbf{x}_A,\mathbf{v}_A,\tau)f(\mathbf{x}_B,\mathbf{v}_B,\tau) - f(\mathbf{x}_C,\mathbf{v}_C,\tau)f(\mathbf{x},\mathbf{v},\tau) \tag{160}$$

The Z_2 part of the collision kernel does not contribute to the collision integral. After doing the delta function integrals over positions $\mathbf{x}_A$, $\mathbf{x}_B$ we obtain

$$\frac{\partial f(\mathbf{x},\mathbf{v},\tau)}{\partial\tau} = \Omega\int [f(\mathbf{x}',\mathbf{v}_A,\tau)f(\mathbf{x},\mathbf{v}_B,\tau) - f(\mathbf{x}',\mathbf{v}_C,\tau)f(\mathbf{x},\mathbf{v},\tau)] \times \Gamma(\mathbf{x},\mathbf{x}')S(\mathbf{v}_A,\mathbf{v}_B;\mathbf{v}_C,\mathbf{v})\mathrm{d}^3\mathbf{v}_A\mathrm{d}^3\mathbf{v}_B\mathrm{d}^3\mathbf{v}_C\mathrm{d}^3\mathbf{x}'. \tag{161}$$

Now we insert $S = S_1 + S_2$ from Eqs. 99 and 100 in this equation. The S_2 part gives no contribution to the integral as before. Doing the integrals over $\mathbf{v}_A,\mathbf{v}_B,\mathbf{v}_C$ in the center of mass coordinates we obtain

$$\frac{\partial f(\mathbf{x},\mathbf{v},\tau)}{\partial \tau}=\frac{\Omega}{R}\int [f(\mathbf{x}',\mathbf{v}_A,\tau)f(\mathbf{x},\mathbf{v}_B,\tau)-f(\mathbf{x}',\mathbf{v}_C,\tau)f(\mathbf{x},\mathbf{v},\tau)] \times \Gamma(\mathbf{x},\mathbf{x}')u\sigma(\mathbf{n},\mathbf{n}')\mathrm{d}^3\mathbf{u}\mathrm{d}\mathbf{n}'\mathrm{d}^3\mathbf{x}'. \quad (162)$$

where $\mathbf{v}_A$, $\mathbf{v}_B$, $\mathbf{v}_C$ are given in Eqs. 89–91. In order to have complete correspondence with the Boltzmann equation we define the new function $F(\mathbf{x},\mathbf{v},\tau) = Nf(\mathbf{x},\mathbf{v},\tau)$, and we also define the new variable $t = \Omega\ \tau/RN = 2\Omega n/RN^2$ to obtain

$$\frac{\partial F(\mathbf{x},\mathbf{v},t)}{\partial t} = \widehat{L}_C F(\mathbf{x},\mathbf{v},t) \quad (163)$$

where the operator $\widehat{L}_C$ is defined as

$$\widehat{L}_C F(\mathbf{x},\mathbf{v},t)=\int [F(\mathbf{x}',\mathbf{v}_A,t)F(\mathbf{x},\mathbf{v}_B,t)-F(\mathbf{x}',\mathbf{v}_C,t)F(\mathbf{x},\mathbf{v},t)] \times \Gamma(\mathbf{x},\mathbf{x}')u\sigma(\mathbf{n},\mathbf{n}')\mathrm{d}^3\mathbf{u}\mathrm{d}\mathbf{n}'\mathrm{d}^3\mathbf{x}'. \quad (164)$$

Here t is interpreted as the physical time.

In the collisions part of the DSMC method we make collision attempts for a time Δt where Δt is a small time interval. This corresponds to $\Delta\tau = RN\Delta t/\Omega$ collision time passage or $\Delta n = RN^2\Delta t/2\Omega$ pairs chosen. From Eq. 163, after making Δn collisions attempt $F(\mathbf{x},\mathbf{v},t)$ becomes $F^*(\mathbf{x},\mathbf{v},t)$

$$F^*(\mathbf{x},\mathbf{v},t) = (1+\Delta t\widehat{L}_C)F(\mathbf{x},\mathbf{v},t) + O((\Delta t)^2) \quad (165)$$

where $O((\Delta t)^2)$ is an error term of order $(\Delta t)^2$.

Next we perform free propagation step where $x \to x + \Delta t\mathbf{v}$ and $\mathbf{v} \to \mathbf{v} + \Delta t\mathbf{a}$ transformation is made for each particle. Here $\mathbf{a}=\mathbf{F}/m$ is the acceleration of the particle due to the force $\mathbf{F}$, and it can depend on both position and velocity of the particle. This changes the N particle distribution function $f^{(N)}(\mathbf{x}_1,\mathbf{v}_1;\mathbf{x}_2,\mathbf{v}_2;\ldots,\mathbf{x}_N,\mathbf{v}_N)$ to

$$f^{(N)}(\mathbf{x}_1-\Delta t\mathbf{v}_1,\mathbf{v}_1-\Delta t\mathbf{a}_1;\ldots;\mathbf{x}_N-\Delta t\mathbf{v}_N,\mathbf{v}_N-\Delta t\mathbf{a}_N). \quad (166)$$

The Jacobian of the transformation is unity with a correction of order $(\Delta t)^2$, and therefore this expression is correct with an error of the same order. Integrating this over $\mathbf{x}_2$, $\mathbf{v}_2$; ..., $\mathbf{x}_N$, $\mathbf{v}_N$ we find that the single particle probability distribution $f^{(1)}(\mathbf{x},\mathbf{v})$ changes to $f^{(1)}(\mathbf{x}-\Delta t\mathbf{v},\mathbf{v}-\Delta t\mathbf{a})$ with an error term of order $(\Delta t)^2$. Therefore $F^*(\mathbf{x},\ \mathbf{v},\ t)$ becomes $F^*(\mathbf{x}-\Delta t\mathbf{v},\ \mathbf{v}-\Delta t\mathbf{a},\ t)$ which is taken as $F(\mathbf{x},\mathbf{v},t+\Delta t)$. Hence

$$F(\mathbf{x},\mathbf{v},t+\Delta t) = F^*(\mathbf{x}-\Delta t\mathbf{v},\mathbf{v}-\Delta t\mathbf{a},t). \quad (167)$$

Using Eq. 165 and expanding $F(\mathbf{x}-\Delta t\mathbf{v},\mathbf{v}-\Delta t\mathbf{a},t)$ up to first order terms in Δt we obtain

$$F(\mathbf{x},\mathbf{v},t+\Delta t) = \left(1-\Delta t\mathbf{v}\frac{\partial}{\partial\mathbf{x}}-\Delta t\mathbf{a}\frac{\partial}{\partial\mathbf{v}}+\Delta t\widehat{L}_C\right)F(\mathbf{x},\mathbf{v},t) + O((\Delta t)^2) \quad (168)$$

where $O((\Delta t)^2)$ is the error terms of order $(\Delta t)^2$. Taking the limit $\Delta t \to 0$ we obtain

$$\frac{\partial F(\mathbf{x},\mathbf{v},t)}{\partial t} + \mathbf{v}\cdot\frac{\partial F(\mathbf{x},\mathbf{v},t)}{\partial\mathbf{x}} + \frac{\mathbf{x}}{m}\cdot\frac{\partial F(\mathbf{x},\mathbf{v},t)}{\partial\mathbf{v}} = \widehat{L}_C F(\mathbf{x},\mathbf{v},t). \quad (169)$$

This equation is similar to the Boltzmann equation but it is not the same. Already when treating $\tau = 2n/N$ as a continuous parameter we took $N\to\infty$ limit implicitly. The remaining limit is $V_k\to 0$ and we know that $\Gamma(\mathbf{x},\mathbf{x}') \to \delta(\mathbf{x}-\mathbf{x}')$ in this limit. After setting $\Gamma(\mathbf{x},\mathbf{x}') = \delta(\mathbf{x}-\mathbf{x}')$ performing the $\mathbf{x}'$ integral the operator $\widehat{L}_C$ reduces to

$$\widehat{L}_C F(\mathbf{x},\mathbf{v}) = \int [F(\mathbf{x},\mathbf{v}_A,t)F(\mathbf{x},\mathbf{v}_B,t) - F(\mathbf{x},\mathbf{v}_C,t)F(\mathbf{x},\mathbf{v},t)]u\sigma(\mathbf{n},\mathbf{n}')\mathrm{d}^3\mathbf{u}\mathrm{d}\mathbf{n}'. \quad (170)$$

With this form of the $\widehat{L}_C$ the Eq. 169 is the Boltzmann equation.

Hence, we have shown that in direct simulation algorithm for inhomogeneous gas the one particle probability distribution satisfies the Boltzmann equation. Now, how do we connect this to the Bird's NTC algorithm? Clearly they are not the same. In fact our algorithm is not practical since great majority of chosen pairs will not be in the same cell and therefore will not make collisions.

In the time interval Δt we choose $\Delta n = RN^2\Delta t/2\Omega$ pairs. The probability that each pair will make a collision attempt in the kth cell is $p_k = (\Omega/V_k)(N_k/N)^2$. Let n_k be the number of collision attempts that take place in V_k. The expected value of n_k is

$$\overline{n}_k = \Delta n\cdot p_k = \frac{RN_k^2}{2V_k}\Delta t. \quad (171)$$

This is the same as number of collision attempts in V_k in Birds algorithm. The difference is that in Birds algorithm the number of collision attempts in each cell is fixed as $n_k = RN_k^2\Delta t/2V_k$ whereas in our algorithm the n_k has a probability distribution with a mean value $RN_k^2\Delta t/2V_k$. The probability distribution for n_k is given as

$$P(n_k) = \frac{(\Delta n)!}{(\Delta n-n_k)!(n_k)!}(p_k)^{n_k}(1-p_k)^{\Delta n-n_k}. \quad (172)$$

In the limit of $V_k\to 0$ we have $p_k\to 0$ and the $P(n_k)$ becomes the Poisson probability distribution

$$P(n_k) = \frac{(\overline{n}_k)^{n_k}}{(n_k)!}\exp(-\overline{n}_k). \quad (173)$$

The width of distributions in Eqs. 172 and 173 is of order $\sqrt{\overline{n}_k}$. For large values of $\overline{n}_k$ we have $n_k/\overline{n}_k = 1 + O(1/\sqrt{\overline{n}_k})$ where $O(1/\sqrt{\overline{n}_k})$ is a term of order $1/\sqrt{\overline{n}_k}$.

Now we take the limit $N_k\to\infty$ and $O(1/\sqrt{\overline{n}_k})$ error term vanishes. In a more mathematical language, probability that $n_k/\overline{n}_k = 1$ is unity. Hence, both methods approach each other in the limit $N_k\to\infty$, and single particle

probability distribution in Bird's method too should satisfy the Boltzmann equation (Eq. 169) in this limit.

There is an important distinction in the limits taken for both methods to satisfy the Boltzmann equation. In our algorithm we take $N\to\infty$, $\Delta t\to 0$ and $V_k\to 0$ limits. This does not mean that number of particles in each cell (N_k) will go to infinity. For example for a uniform density we have $N_k = (N/V)V_k$. Here $N\to\infty$ and $V_k\to 0$ limits does not imply anything about N_k. NV_k can remain finite and even can go to zero, and still our algorithm satisfies the Boltzmann equation. The Bird's algorithm requires $N_k\to\infty$ to satisfy the Boltzmann equation; however, this is a more stringent requirement.

We did this analysis for the simplest case of one species of gas molecules without internal degrees of freedom for clarity. It is very simple to generalize this to the other cases by replacing the kernel S in Eq. 154 with G^{rs}_{pq} in Eq. 112 or with $K^{\alpha\beta}_{ij}$ in Eq. 128 or with $Q^{\alpha\beta,rs}_{ij,pq}$ in Eq. 135. Then the Boltzmann equation will be replaced by the Wang Chang–Uhlenbeck equation but all of the arguments will remain the same.

5 Conclusions

Let us list our contributions in this paper.

- In this paper we introduced a general formalism for direct simulation processes. We defined the direct simulation as a Markov process with a master equation and we found the master equation given in Eq. 9. Defining the DSMC algorithm as a stochastic process governed by a master equation does not exist in the literature of the DSMC method to our knowledge.
- Starting from the master equation we showed that the N-particle probability density evolves towards micro-canonical distribution as the number of collisions go to infinity.
- We derived a hierarchy of equations similar to the BBGKY hierarchy for the reduced probability densities given in Eq. 25.
- We showed that if AMC approximation is employed the single particle probability distribution satisfies an equation given in Eq. 29. In the limit $N\to\infty$ this reduces to Eq. 31, which is an equation similar to the Boltzmann equation.
- We found the equations of the hierarchy in the limit $N\to\infty$ (Eq. 35) and showed that the Ansatz $f^{(M)}(\mu_1,\mu_2,\ldots,\mu_M;\tau) = f^{(1)}(\mu_1;\tau)f^{(1)}(\mu_2;\tau)\ldots f^{(1)}(\mu_M;\tau)$ satisfies all the equations in the hierarchy provided the $f^{(1)}(\mu;\tau)$ satisfies the Eq. 31. This ensures that in the limit $N\to\infty$ the AMC is satisfied for all times if one starts from an uncorrelated initial state.
- We gave two simple examples from direct simulation money games. The discrete money game example has the nice feature that it is exactly solvable, and we observe from the solution that the approach to the equilibrium is exponentially fast.
- We obtained the H-theorem and conservation of expectation values of collision invariants. These results are familiar to most readers from the standard treatments of the Boltzmann equation. But it is worth repeating them here because although the equations are similar they are applied to wide variety of different problems in the direct simulation setting, not just to gases.
- We applied the formalism to the direct simulation Monte Carlo method for real homogenous gases which is a standard method to solve the Boltzmann equation. Introducing appropriate kernels we obtained NTC algorithm for a homogenous gas, and we showed that the appropriately normalized single particle probability distribution satisfies Boltzmann equation for simple homogenous gases and Wang Chang–Uhlenbeck equations for homogenous molecular gases and their mixtures. The derivation of conservation of $\int f^p(\mathbf{v})\,\mathrm{d}^3\mathbf{v}$ for mixture of gases without internal degrees of freedom and $\sum_i \int f_i^p(\mathbf{v})\mathrm{d}^3\mathbf{v}$ for mixture of gases with internal degrees of freedom should be also familiar to the reader from the standard treatments of the Boltzmann equation. The novel feature of our derivation is the significant simplification that the normalization of $T(\mu_A,\ \mu_B,\ \mu_C,\ \mu_D)$ given in the Eqs. 3, 123, 124, 145 and 146 provide to obtain the result. If we try to obtain the same result from the Boltzmann equation we would have to use the argument that the integrals in Eqs. 123, 124, 145 and 146 are functions of the collision invariants.
- We introduced a new algorithm to do the DSMC calculations for an inhomogeneous gas. Our algorithm is not practical for the actual practice of the art because of wasting the great majority of the chosen pairs. We showed that the single particle probability distribution satisfies the Boltzmann equation in our algorithm in the limits $N\to\infty$, $\Delta t\to 0$ and $V_k\to 0$. We also showed that Bird's algorithm for DSMC converges to our algorithm if $N_k\to\infty$ is taken in addition to the limits $\Delta t\to 0$ and $V_k\to 0$. Birds algorithm requires more stringent requirements to satisfy the Boltzmann equation. To prevent any misunderstanding we stress here that our algorithm is not intended as a practical scheme to implement DSMC calculations. The Bird's algorithm does not easily fit in the direct simulation formalism presented in this paper whereas the algorithm we presented does. We showed that our algorithm gives the Boltzmann

equation in the limits $N\to\infty$, $\Delta t\to 0$ and $V_k\to 0$, and we also showed that our algorithm and Bird's algorithm converge to each other if we go to more stringent limit of $N_k\to\infty$. Therefore we proved indirectly that Birds algorithm satisfies Boltzmann equation in the limit $N_k\to\infty$, $\Delta t\to 0$ and $V_k\to 0$. Therefore we introduced our algorithm as a tool to study convergence of Bird's method, and not as a practical way of doing DSMC calculations.

Finally, we would like to comment on educational use of the direct simulation Monte Carlo methods. We got involved in this subject through the computational statistical physics projects we assigned to advanced undergraduates over the last several years. We found direct simulation algorithms very effective to attract students interest in the subject. After the students finish their projects and observe that the system evolves towards the equilibrium distribution, there comes the point that they want to know why it works. There are heuristic explanations as in the Bird's original papers, and there are very formal and difficult to read convergence proofs written by mathematicians available to answer their worries. Our motivation in this research was to invent a satisfactory, rigorous and simple explanation we could give to our students (or students and instructors elsewhere). As a first product of our efforts in this direction, a simplified version of this paper [17] containing only one kind of homogenous gas without internal degrees of freedom is published in *American Journal of Physics*. As we extended our student project to gases with internal states and mixture of gases, the results in this paper evolved.

This work can generalize to chemical reactions and radiative processes in a more or less straightforward fashion. But there are enough number of subtleties such that we leave them to future publications.

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