

ENERGY CONSERVING DISCRETE BOLTZMANN EQUATION FOR NONIDEAL SYSTEMS

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The BBGKY formalism is utilized to obtain a set of moment equations to be satisfied by the collision operator in an energy conserving discrete Boltzmann equation for the case of a nonlocal interaction potential. A modified BGK form of the collision operator consistent with these moment equations is described. In the regime of isothermal flows, a previous proposed nonideal gas model is recovered. Other approaches to constructing the collision operator are discussed. Numerical implementation of the modified BGK form, using a thermal lattice Boltzmann model, is illustrated as an example. The time dependence of the density autocorrelation function was studied for this model and found, at early times, to be strongly affected by the constraint of total energy conservation. The long time behavior of the density autocorrelation function was consistent with the theory of hydrodynamic fluctuations.

Keywords: BBGKY; BGK; Discrete Boltzmann Methods; Hydrodynamic Fluctuations; Lennard-Jones Fluid; Nonideal Systems; Thermal Lattice Boltzmann.

1. Introduction

Discrete Boltzmann methods have emerged as a powerful technique for the computational modeling of a wide variety of complex fluid flow problems including single and multiphase flow in complex geometries.¹⁻⁷ While much progress has been made in the construction of discrete Boltzmann based models that describe single phase fluid flow with heat transport, isothermal fluids that undergo liquid/vapor phase transitions, and the phase separation of binary mixtures, until now no self-consistent model exists that conserves energy when a molecular interaction potential is included. Some computational fluid dynamics (CFD) based algorithms,⁸ which describe nonideal gas systems, can be explicitly constructed to conserve mass, momentum, and energy. However, in this case, information about the effects of molecular interactions are incorporated into a modified stress tensor that is derived from a phenomenological Cahn Hilliard free energy which is typically expressed in terms of an expansion of density and density gradients.

In this paper it will be shown how energy conservation for a nonideal system can be incorporated into a discrete Boltzmann model. The basic idea is to properly construct the collision operator, used in the discrete Boltzmann equations, so as to account for momentum and energy transfer due to a molecular interactions. Information about momentum and energy transfer can be directly obtained from the Bogoliubov–Born–Green–Kirkwood–Yvon (BBGKY)^{9,10} formalism. This method should serve as an ideal mesoscopic approach that bridges microscopic phenomena with the continuum macroscopic equations. Further, it can be directly implemented as a numerical method to model the time evolution of such systems.

An outline of this paper goes as follows. First, pertinent results obtained from the BBGKY equations will be reviewed including construction of moments of the collision operator and demonstration of energy conservation. A modified Bhatnagar, Gross and Krook¹¹ (BGK) representation of the collision operator that is consistent with energy conservation will then be described. An earlier model of Shan and Chen⁴ describing an isothermal nonideal gas as well as other mean-field approaches to modeling nonideal systems, will be shown to be consistent with this formalism. A more general Hermite polynomial¹² representation of the collision operator will be presented and shown to be consistent with the modified BGK form up to 2nd order. An example of a numerical implementation of the modified BGK form will be given. The paper will conclude with a discussion concerning methods for further improvement of the numerical implementation and of other potential applications.

2. The BBGKY Hierarchy

Consider the first two equations associated with the BBGKY hierarchy¹³ which describe the time evolution of single and two particle distribution functions $P_1(\mathbf{r}, \mathbf{k}, t)$ and $P_2(\mathbf{r}_1, \mathbf{k}_1, \mathbf{r}_2, \mathbf{k}_2, t)$.

$$\partial_t P_1 + \mathbf{k}_1 \cdot \nabla P_1 + \mathbf{F} \cdot \nabla_{\mathbf{k}} P_1 = \Omega, \quad (1)$$

$$\begin{aligned} \partial_t P_2 + \left(\frac{\mathbf{k}_1}{m} \cdot \frac{\partial}{\partial \mathbf{r}_1} + \frac{\mathbf{k}_2}{m} \cdot \frac{\partial}{\partial \mathbf{r}_2} \right) P_2 - \Theta_{12} P_2 \\ = \int d^3 r_3 d^3 k_3 (\Theta_{13} + \Theta_{23}) P_3(\mathbf{r}_1, \mathbf{k}_1, \mathbf{r}_2, \mathbf{k}_2, \mathbf{r}_3, \mathbf{k}_3, t) \end{aligned} \quad (2)$$

where

$$\Theta_{ij} = \frac{\partial V(r_{ij})}{\partial \mathbf{r}_i} \frac{\partial}{\partial \mathbf{k}_i} + \frac{\partial V(r_{ij})}{\partial \mathbf{r}_j} \frac{\partial}{\partial \mathbf{k}_j} \quad (3)$$

P_3 is the three particle distribution function, F is an external force, k_1 is the microscopic momentum, t is time, V is the interparticle potential, and the collision

term Ω is

$$\Omega = - \int d^3 k_2 d^3 r_2 \frac{\partial P_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{k}_1, \mathbf{k}_2, t)}{\partial \mathbf{k}_1} \cdot \frac{\partial V(r_{12})}{\partial \mathbf{r}_1} \quad (4)$$

with $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$.

In the BBGKY hierarchy of equations the time evolution of a single particle distribution is expressed in terms of the two particle distribution function and so forth. Solving for the one through n particle distribution functions involves approximating the form of the $n+1$ particle distribution function to obtain closure of the hierarchy. A variety of techniques and approximations have been developed to obtain closure,¹⁴ some of which are mentioned later in this paper.

2.1. Moments of collision term

Consider moments of Ω which are related to conserved quantities.

$$\int d^3 k_1 C(\mathbf{r}_1, \mathbf{k}_1, t) \Omega = - \int d^3 k_1 d^3 r_2 d^3 k_2 P_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{k}_1, \mathbf{k}_2, t) \frac{\partial C}{\partial \mathbf{k}_1} \cdot \frac{\partial V(r_{12})}{\partial \mathbf{r}_1} \quad (5)$$

where C is a function of position or momentum. Here we have integrated by parts and assumed that P_2 goes to zero in the limit of large k .

For C equal to a constant the integral in Eq. (5) is equal to zero corresponding to conservation of mass. For the momentum moment ($C = \mathbf{k}$) we have

$$\begin{aligned} \int d^3 k_1 \mathbf{k}_1 \Omega &= - \int d^3 k_1 d^3 r_2 d^3 k_2 P_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{k}_1, \mathbf{k}_2, t) \frac{\partial \mathbf{k}_1}{\partial \mathbf{k}_1} \cdot \frac{\partial V(r_{12})}{\partial \mathbf{r}_1} \\ &= - \int d^3 r_2 P_2(\mathbf{r}_1, \mathbf{r}_2, t) \frac{\partial V(r_{12})}{\partial \mathbf{r}_1} \end{aligned} \quad (6)$$

where $P_2(\mathbf{r}_1, \mathbf{r}_2, t) = \int d^3 k_1 d^3 k_2 P_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{k}_1, \mathbf{k}_2, t)$.

The kinetic energy moment ($C = k^2/2m$) is

$$\int d^3 k_1 \frac{k_1^2}{2m} \Omega = - \int d^3 k_1 d^3 r_2 d^3 k_2 P_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{k}_1, \mathbf{k}_2, t) \frac{\mathbf{k}_1}{m} \cdot \frac{\partial V(r_{12})}{\partial \mathbf{r}_1}. \quad (7)$$

In the regime of low to moderate densities where multiple collisions between atoms can be ignored the molecular chaos approximation is valid.^{10,15} Here

$$P_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{k}_1, \mathbf{k}_2) = P_1(\mathbf{r}_1, \mathbf{k}_1) P_1(\mathbf{r}_2, \mathbf{k}_2) g(\mathbf{r}_1, \mathbf{r}_2)$$

and $g(\mathbf{r}_1, \mathbf{r}_2)$ is the two point correlation function. Then Eqs. (6) and (7) become

$$\partial_t \mathbf{P} = \int d^3 k_1 \mathbf{k}_1 \Omega = - P_1(\mathbf{r}_1) \int d^3 r_2 P_1(\mathbf{r}_2) g(\mathbf{r}_1, \mathbf{r}_2) \frac{\partial V(r_{12})}{\partial \mathbf{r}_1} \quad (8)$$

and

$$\partial_t E_{ke} = \int d^3 k_1 \frac{k_1^2}{2m} \Omega = - P_1(\mathbf{r}_1) \int d^3 r_2 P_1(\mathbf{r}_2) g(\mathbf{r}_1, \mathbf{r}_2) \mathbf{v}_1 \cdot \frac{\partial V(r_{12})}{\partial \mathbf{r}_1}. \quad (9)$$

For the case of nonlocal interactions neither the momentum or energy are conserved at a point as a fluid region responds to the forces from neighboring areas. Equations (8) and (9) respectively represent the change of momentum and the rate work is done on the fluid due to an effective averaged force field. Note that the moments depend on the two point correlation function. As mentioned above, this function could in principle be approximated by solving a closed set of the BBGKY hierarchy of equations. For this paper we will assume that $g(\mathbf{r}_1, \mathbf{r}_2)$ or, for that matter, $g(\mathbf{r}_1, \mathbf{r}_2, \mathbf{k}_1, \mathbf{k}_2)$ is known or can be obtained by other simulation techniques like molecular dynamics.^{16,17}

While momentum and energy are not conserved locally, they are conserved globally. For example, to show that total energy is globally conserved, first note that the local potential energy is given by

$$\phi(r) = \frac{1}{2} \int d^3r_1 d^3r_2 P(\mathbf{r}_1, \mathbf{r}_2, t) \delta^{(3)}(\mathbf{r}_1 - \mathbf{r}) V(r_{12}).$$

The total energy, E , of this system is then given by the volumetric integral of the kinetic and potential energy,

$$E = \int d^3r d^3k \frac{k^2}{2m} P_1(\mathbf{r}, \mathbf{k}) + \frac{1}{2} \int d^3r d^3r_1 d^3r_2 P(\mathbf{r}_1, \mathbf{r}_2, t) \delta^{(3)}(\mathbf{r}_1 - \mathbf{r}) V(r_{12}). \quad (10)$$

The time derivative of the local potential energy can be obtained from the BBGKY equations since

$$\partial_t \phi(r) = \frac{1}{2} \int d^3r_1 d^3r_2 \partial_t P(\mathbf{r}_1, \mathbf{r}_2, t) \delta^{(3)}(\mathbf{r}_1 - \mathbf{r}) V(r_{12})$$

so that we can utilize Eq. (2). Terms with Θ_{ij} integrate out to zero. Integration by parts of the remaining terms obtains

$$\begin{aligned} \partial_t \phi(r) &= \frac{1}{2} \int d^3r_1 d^3k_1 d^3r_2 d^3k_2 \delta(\mathbf{r}_1 - \mathbf{r}) P_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{k}_1, \mathbf{k}_2, t) \\ &\quad \times \left(\frac{\mathbf{k}_1}{m} \cdot \frac{\partial V(r_{12})}{\partial \mathbf{r}_1} + \frac{\mathbf{k}_2}{m} \cdot \frac{\partial V(r_{12})}{\partial \mathbf{r}_2} \right) \\ &\quad - \frac{1}{2} \nabla \cdot \int \int d^3r_1 d^3k_1 d^3r_2 d^3k_2 \mathbf{k}_1 V(r_{12}) P_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{k}_1, \mathbf{k}_2, t). \end{aligned}$$

It is then easy to see that

$$\int d^3r \partial_t \phi = - \int d^3r \partial_t E_{ke}$$

thus proving global conservation of energy.

In addition, it can be shown that⁹ $\partial_t \mathbf{P}$ and $\partial_t E_{ke} + \partial_t \phi$ can be written as the divergence of a function so that, in a numerical implementation, total momentum and energy are easily conserved in a closed system.

Here the momentum moment of the collision operator is written as

$$\int d^3k k \mathbf{k} \Omega = -\nabla \cdot \frac{1}{2} \int d^3r_1 d^3r_2 \delta^3(\mathbf{r}_1 - \mathbf{r}) \mathbf{r}_{12} \hat{\tau}_{12} \frac{\partial V(\mathbf{r}_{12})}{\partial \mathbf{r}_{12}} \times \left[\sum_{n=1}^{\infty} \frac{1}{n!} (-\mathbf{r}_{12} \cdot \nabla_{\mathbf{r}_1})^{n-1} \right] P(\mathbf{r}_1, \mathbf{r}_1 + \mathbf{r}_{12}) \quad (11)$$

and the kinetic energy moment is

$$\int d^3k \frac{k^2}{2m} \Omega = -\partial_t \phi - \nabla \cdot (\phi \mathbf{v}) - \nabla \cdot \frac{1}{2} \int d^3r_1 d^3k_1 d^3r_2 d^3k_2 P_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{k}_1, \mathbf{k}_2) \delta^3(\mathbf{r}_1 - \mathbf{r}) V(\mathbf{r}_{12}) \times \left(\frac{\mathbf{k}_1}{m} - \mathbf{v} \right) + \frac{1}{2} \nabla \cdot \int d^3r_1 d^3k_1 d^3r_{12} d^3k_2 \delta^3(\mathbf{r}_1 - \mathbf{r}) \frac{\partial V(\mathbf{r}_{12})}{\partial \mathbf{r}_{12}} \mathbf{r}_{12} \times \left(\hat{\tau}_{12} \cdot \frac{\mathbf{k}_1}{m} \right) \left[\sum_{n=1}^{\infty} \frac{1}{n!} (-\mathbf{r}_{12} \cdot \nabla_{\mathbf{r}_1})^{n-1} \right] P(\mathbf{r}_1, \mathbf{r}_1 + \mathbf{r}_{12}, \mathbf{k}_1, \mathbf{k}_2). \quad (12)$$

In the limit of small variation of P_2 over a range $L \gg r_{12}$, where L is the characteristic length of density fluctuation, terms with $n > 1$ can be ignored. Then

$$\int d^3k k \mathbf{k} \Omega \simeq -\nabla \cdot \left[\frac{1}{2} \int d^3r_1 d^3r_2 \delta^3(\mathbf{r}_1 - \mathbf{r}) \mathbf{r}_{12} \hat{\tau}_{12} \frac{\partial V(\mathbf{r}_{12})}{\partial \mathbf{r}_{12}} P(\mathbf{r}_1, \mathbf{r}_2) \right]$$

or

$$\int d^3k k \mathbf{k} \Omega \simeq -\nabla \cdot \overleftrightarrow{B}. \quad (13)$$

Similarly, for the kinetic energy moment, including the $n = 1$ term only obtains

$$\int d^3k_1 \frac{k_1^2}{2m} \Omega \simeq -\partial_t \phi - \nabla \cdot (\phi \mathbf{v}) - \nabla \cdot (\overleftrightarrow{B} \cdot \mathbf{v} + \mathbf{q}_v) \quad (14)$$

where

$$\mathbf{q}_v(\mathbf{x}, t) = \frac{1}{2} \int d^3r_1 d^3r_2 d^3k_1 d^3k_2 P(\mathbf{r}_1, \mathbf{r}_2, \mathbf{k}_1, \mathbf{k}_2, t) \delta^{(3)} \times (\mathbf{r}_1 - \mathbf{r})(\mathbf{k}_1/m - \mathbf{v}) \cdot (V(\mathbf{r}_{12}) \overleftrightarrow{\mathbf{1}} - V'(\mathbf{r}_{12}) \mathbf{r}_{12}^{-1} \mathbf{r}_{21} \mathbf{r}_{21}). \quad (15)$$

Using the molecular chaos approximation

$$B_{i,j}(\mathbf{r}, t) = -\frac{1}{2} \int d^3r_1 d^3r_2 P_1(\mathbf{r}_1) P_1(\mathbf{r}_2) \delta^{(3)} \times (\mathbf{r}_1 - \mathbf{r}) g(\mathbf{r}_1, \mathbf{r}_2) V'(\mathbf{r}_{12}) \mathbf{r}_{12}^{-1} (\mathbf{r}_{21})_i (\mathbf{r}_{21})_j \quad (16)$$

and $\mathbf{q}_v = 0$ indicating that without velocity correlations, currents associated with potential energy are zero.

Again, since only the divergence of \vec{B} and \mathbf{q}_v are present in Eqs. (13) and (14), it is easy to numerically implement momentum and energy conservation.

For later reference the collision operator moments are summarized below.^{9,10}

$$\int d^3\mathbf{k}\Omega = 0, \quad (17a)$$

$$\int d^3\mathbf{k}\mathbf{k}\Omega = -\nabla \cdot \vec{W}, \quad (17b)$$

$$\int d^3\mathbf{k}\frac{k^2}{2m}\Omega = -\partial_t\phi - \nabla \cdot (\phi\mathbf{v}) - \nabla \cdot \mathbf{Z} \quad (17c)$$

where $-\nabla \cdot \vec{W}$ is equal to the righthand side of Eq. (11) and $-\nabla \cdot \mathbf{Z}$ is equal to the last two terms on the righthand side of Eq. (12). This represents a "conservative" form of the moment equations. In the case of $n = 1$ only, $\vec{W} = \vec{B}$ and $\mathbf{Z} = \vec{B} \cdot \mathbf{v} + \mathbf{q}_v$.

3. Modified BGK Form of Collision Term

With the basic equations and methodology for obtaining moments of the collision operator laid out, a modified BGK form of the collision term is suggested:

$$\Omega = -\frac{1}{\lambda}(P - P^{eq}). \quad (18)$$

Here we take the "equilibrium" distribution, P^{eq} to have the following form:

$$P^{eq} = \frac{n'}{(2\pi mKT')^{D/2}} \exp\left(-\frac{(\mathbf{k} - \mathbf{k}')^2}{2mKT'}\right) \quad (19)$$

and n' , \mathbf{k}' , and T' are determined by the moment equations.

Using the modified BGK collision operator in Eq. (17a) gives $n' = n$ (the number of particles per unit volume). The momentum moment of Eq. (18) obtains:

$$\int d^3\mathbf{k}\mathbf{k}\Omega = -\int d^3\mathbf{k}\mathbf{k}\frac{1}{\lambda}(P - P^{eq}) = -\frac{n}{\lambda}(\langle\mathbf{k}\rangle - \mathbf{k}') = -\frac{\rho}{\lambda}(\mathbf{v} - \mathbf{v}') \quad (20)$$

where $\mathbf{v} = \langle\mathbf{k}\rangle/m$ is the average velocity and $\rho = mn$ is the density. Then Eq. (17b) implies

$$\mathbf{v}' = \mathbf{v} - \frac{\lambda}{\rho}\nabla \cdot \vec{W}. \quad (21)$$

Finally noting that the kinetic energy moment of P^{eq} is

$$\int d^3\mathbf{k}\frac{k^2}{2m}P^{eq} = \frac{3\rho KT'}{2m} + \frac{1}{2}\rho v'^2, \quad (22)$$

Eq. (17c) gives

$$KT' = \frac{2m\lambda}{3\rho}(-\partial_t\phi - \nabla \cdot (\phi\mathbf{v}) - \nabla \cdot \mathbf{Z}) + \frac{m}{3}(\langle v^2 \rangle - v'^2). \quad (23)$$

Hence to preserve global energy conservation the local temperature must be rescaled.

In addition, this modified BGK form, in the isothermal limit, can recover the Shan Chen⁴ model where, as in Eq. (21), the equilibrium velocity is shifted to account for nonlocal interactions. In their model, \overleftrightarrow{W} was approximated by an effective potential which is a function of density:

$$\nabla \cdot \overleftrightarrow{W} \simeq \nabla V(\rho(\mathbf{x}_1), \rho(\mathbf{x}_2)). \quad (24)$$

The modified BGK collision operator [Eq. (19)] can now be incorporated into a discrete Boltzmann model for numerical simulation by, for example, expanding P^{eq} in terms of Hermite polynomials and discretizing the velocity space by quadrature methods.¹² Similarly, other realizations of a thermal equilibrium distribution can be easily adopted to this approach by appropriately shifting the velocity and temperature in a manner described above.

While the above modified BGK formalism can accommodate the three conserved quantities: mass, momentum, and energy, information from other moments of the collision operator may not be present. For example, correlations in the velocity field are not properly accounted for in the Gaussian form of the equilibrium distribution. Extra constraints may be accounted for in a more general locally anisotropic “equilibrium” distribution the ES or ellipsoidal statistical model.¹⁸

$$P_{\text{es}}^{\text{eq}} = n \frac{\sqrt{\det A}}{\pi^{\frac{3}{2}}} \exp[-A_{ij}(k_i - k'_i)(k_j - k'_j)].$$

The A_{ij} are determined from the 2nd order moment equations. Note, the ES distribution was originally used to model systems with variable Prandtl number.¹⁸

For the case when the molecular chaos approximation is valid, the moment

$$\int d^3k k_i k_j \Omega = -m \int d^3r_1 P(\mathbf{r}) P(\mathbf{r}_1) g(\mathbf{r}, \mathbf{r}_1) \frac{\partial V(R)}{\partial \mathbf{r}_1} \times [(\delta_{1i} v_j + \delta_{1j} v_i) \hat{i} + (\delta_{2i} v_j + \delta_{2j} v_i) \hat{j} + (\delta_{3i} v_j + \delta_{3j} v_i) \hat{k}] \quad (25)$$

may be properly accounted for in the BGK form.

4. Alternate Methods of Representing Collision Term

The collision term Ω may be represented as a Hermite expansion^{12,15,19} $\xi = k/m$:

$$\Omega = \omega(\xi) \sum_{n=0}^{\infty} \frac{1}{n!} \rho^{(n)}(\mathbf{x}, t) \mathcal{H}^{(n)}(\xi), \quad (26)$$

where the weight function

$$\omega(\xi) = (1/2\pi)^{D/2} \exp(-\xi^2/2). \quad (27)$$

Here, the microscopic velocity, ξ is in units of $c_o = \sqrt{KT_o/m_o}$ and T_o and m_o are units of the temperature and mass respectively. A dimensionless temperature

may be represented by $\theta = Tm_o/T_o m$. Readers are referred to Refs. 7 and 12 for more background and details. The generalized Hermite polynomials $\{\mathcal{H}^{(n)}\}$ form a complete ortho-normal basis in ξ -space with respect to the weight function $\omega(\xi)$:

$$\int d\xi^3 \omega(\xi) \mathcal{H}_i^{(m)} \mathcal{H}_j^{(n)} = \delta_{mn} \delta_{ij}, \quad (28)$$

where $\mathbf{i} \equiv (i_1, i_2, \dots, i_m)$, $\mathbf{j} \equiv (j_1, j_2, \dots, j_n)$, and $\delta_{ij} = 1$ when \mathbf{j} is a permutation of \mathbf{i} , and $\delta_{ij} = 0$ otherwise. Thus the coefficients $\mathbf{p}^{(n)}$ can be determined from the above orthogonal relation [Eq. (28)]:

$$\mathbf{p}^{(n)} = \int d\xi \mathcal{H}^{(n)} \Omega. \quad (29)$$

The generalized Hermite polynomial $\mathcal{H}^{(n)}$ and coefficient $\mathbf{p}^{(n)}$ in the expansion are symmetric tensors of rank n . An element of these tensors is denoted by the same symbol, $\mathcal{H}^{(n)}$ or $\mathbf{p}^{(n)}$, with n subscripts for $n \geq 1$. And in the case of $n = 0$, the subscript is omitted. The product $\mathbf{p}^{(n)} \mathcal{H}^{(n)}$ denote contraction on all the n subscripts. The first three generalized Hermite polynomials are

$$\mathcal{H}^{(0)} = 1, \quad (30a)$$

$$\mathcal{H}_i^{(1)} = \xi_i, \quad (30b)$$

$$\mathcal{H}_{ij}^{(2)} = \xi_i \xi_j - \delta_{ij}. \quad (30c)$$

The $\mathbf{p}^{(n)}$ may be directly obtained, to any order, from the moment equations where $p^0 = 0$, $p^1 = \nabla \cdot \vec{W}$ and so forth. When expanding P and P^{eq} in Hermite polynomials the modified BGK form is found to be equivalent, to second order, to Hermite representation of the collision operator [Eq. (26)] when derived from the moments associated with conserved quantities because the first two moments of P are the same as the unscaled equilibrium distribution. Because the Hermite expansion is orthonormal, higher order terms will not directly affect the conserved quantities associated with the first and second moments.

Since the BGK formalism lends itself to analysis of the hydrodynamic limit, another useful form of the collision operator is

$$\Omega = -\frac{1}{\lambda} (P - P^{eq}) + \omega(\xi) \sum_{n=0}^{\infty} \frac{1}{n!} \psi^{(n)}(\mathbf{x}, t) \mathcal{H}^{(n)}(\xi). \quad (31)$$

In this case, the mean velocity and temperature in the equilibrium distribution are not rescaled. The $\psi^{(n)}$ would be determined by the moment equations. A similar form has been suggested in regards to the revised Enskog kinetic theory (RET).²⁰ Note, the RET is limited to the case of hard sphere collisions so that all the energy is kinetic. However, it should be pointed out that there is a potential energy current associated with the transfer of energy due to collisions.

It is easy to see the relation between the BGK form with correction terms [Eq. (31)] and the modified BGK [Eq. (18)] form by expanding $P^{eq'}$ about the microscopic velocity ξ and temperature. First write

$$P^{eq'} = \frac{n}{(2\pi R(T + \Delta T))^{D/2}} \exp\left(-\frac{(\xi + \mathbf{u})^2}{2R(T + \Delta T)}\right). \quad (32)$$

Here $\mathbf{u} = -\mathbf{v}' = -(\mathbf{v} + \Delta\mathbf{u})$ with $\Delta\mathbf{u} = -(\lambda/\rho)\nabla \cdot \vec{W}$, and

$$\Delta T = T' - T = \frac{2\lambda}{3\rho}(-\partial_t\phi - \nabla \cdot (\phi\mathbf{v}) - \nabla \cdot \mathbf{Z}) - \frac{1}{3R}(2\Delta\mathbf{u} \cdot \mathbf{v} + \Delta\mathbf{u}^2). \quad (33)$$

Note, in this example, ξ is *not* rescaled in units of $c_o = \sqrt{KT_o/m_o}$. Next, expand $P^{eq'}$ to second order in velocity and first order in temperature,

$$\frac{P^{eq'}}{n} \approx \omega + \mathbf{u} \cdot \frac{\partial\omega}{\partial\xi} + \Delta T \frac{\partial\omega}{\partial T} + \frac{1}{2}u_i u_j \frac{\partial^2\omega}{\partial\xi_i \partial\xi_j} + \dots$$

where $\omega(\xi, T) = (1/(2\pi RT)^{3/2}) \exp(-\xi^2/2RT)$. Separating terms with ΔT and $\Delta\mathbf{u}$, we can then write the collision operator Ω [Eq. (18)] as

$$\begin{aligned} \Omega = & -\frac{1}{\lambda}(P - P^{eq'}) \approx -\frac{1}{\lambda} \left(P - n\omega \left(1 + \frac{\mathbf{v} \cdot \xi}{RT} + \frac{1}{2} \frac{v_i v_j}{RT} \left(-\delta_{ij} + \frac{\xi_i \xi_j}{RT} \right) \right) \right) \\ & + n \frac{\omega}{\lambda} \frac{\Delta\mathbf{u} \cdot \xi}{RT} + n \frac{\omega}{2\lambda} \frac{\Delta u_i v_j + v_i \Delta u_j + \Delta u_i \Delta u_j}{RT} \left(-\delta_{ij} + \frac{\xi_i \xi_j}{RT} \right) \\ & + n \frac{\omega}{2\lambda} \frac{\Delta T}{T} \left(-\delta_{ii} + \frac{\xi_i \xi_i}{RT} \right). \end{aligned} \quad (34)$$

Equation (34) can be written as

$$\Omega \approx -\frac{1}{\lambda}(P - P^{eq'}) + \Omega'$$

where

$$P^{eq'} \approx n\omega \left(1 + \frac{\mathbf{v} \cdot \xi}{RT} + \frac{1}{2} \frac{v_i v_j}{RT} \left(-\delta_{ij} + \frac{\xi_i \xi_j}{RT} \right) \right)$$

and Ω' can be identified with the Hermite expansion in Eq. (31). Indeed, this expansion still satisfies the moment Eqs. (17a)-(17c) so that mass, momentum and energy are conserved.

Similar results were obtained by considering a Hermite expansion expressed as a function of the peculiar velocity, ($\mathbf{c} = \xi - \mathbf{v}$), instead of the microscopic velocity ξ . Here $P^{eq'}$ was written as

$$P^{eq'} = \frac{n}{(2\pi R(T + \Delta T))^{D/2}} \exp\left(-\frac{(\mathbf{c} + \Delta\mathbf{u})^2}{2R(T + \Delta T)}\right).$$

Again the moment Eqs. (17a)–(17c) were satisfied when expanding to order Δu^2 and ΔT .

A minimal version of Ω' that satisfies the moment Eqs. (17a)–(17c) is

$$\Omega' = -\frac{\omega \nabla \cdot \vec{W} \cdot \xi}{mRT} - \frac{\omega}{3mRT} (+\partial_t \phi + \nabla \cdot (\phi \mathbf{v}) + \nabla \cdot \mathbf{Z}) \left(-\delta_{ii} + \frac{\xi_i \xi_i}{RT} \right).$$

However to be consistent with the moments of the collision operator described in Eq. (25), the collision operator should also include the terms with $\Delta u_i v_j$ as found in the expansion of the modified BGK form.

4.1. Mean-field approaches

Here it is useful to discuss mean field models of nonideal systems. First, returning to the BBGKY collision operator [Eq. (4)] and making the molecular chaos approximation we have

$$\Omega = -\frac{\partial P_1(\mathbf{r}_1, \mathbf{k}_1, t)}{m \partial \mathbf{k}_1} \int d^3 r_2 \rho(\mathbf{r}_2, t) g(\mathbf{r}_1, \mathbf{r}_2, t) \frac{\partial V(r_{12})}{\partial \mathbf{r}_1}. \quad (35)$$

This approximation of the collision operator is of the form of the body force term, $F \cdot \nabla_{\mathbf{k}} P_1$ in Eq. (1). Absorbing the collision term into the body force is called the Vlasov approximation. For $|\mathbf{r}_1 - \mathbf{r}_2| > d$ where d is of order a few “effective” hard sphere diameters, $g(\mathbf{r}_1, \mathbf{r}_2) \approx 1$. After expanding ρ about \mathbf{r}_1 , the contribution to the collision operator associated with the attractive intermolecular interaction, Ω_m can be approximated by, $\Omega_m = \nabla V_m \cdot \nabla_{\mathbf{k}} P_1$, where $V_m = 2a\rho(\mathbf{r}_1) + \kappa \nabla^2 \rho(\mathbf{r}_1)$ with $a = (1/2) \int_d d^3 r V(r)$ and $\kappa = (1/6) \int_d d^3 r r^2 V(r)$. V_m can be thought of as a mean field potential produced by neighboring particles and $-\nabla V_m$ is the associated mean-field force. Note that this approximation of V_m ignores corrections due to spatial gradients in $g(\mathbf{r}_1, \mathbf{r}_2)$, which implicitly depends on \mathbf{r} through the interaction potential and temperature field. The contribution of this attractive intermolecular interaction to the pressure tensor can be written as

$$\vec{B}_m = \left[-a\rho^2 + \kappa \left(\frac{1}{2} |\nabla \rho|^2 + \rho \nabla^2 \rho \right) \right] \mathbf{I} - \kappa \nabla \rho \nabla \rho.$$

This form of pressure tensor has been explored²⁴ for the case of isothermal systems. A second contribution to the forcing, Ω_r , is due to the repulsion of molecules and corresponds to evaluation of the collision operator for $|\mathbf{r}_1 - \mathbf{r}_2| < d$.

$$\Omega_r = -\frac{\partial P_1(\mathbf{r}_1)}{\partial \mathbf{k}_1} \int^{|\mathbf{r}_1 - \mathbf{r}_2| < d} d^3 r_2 \rho(\mathbf{r}_2, t) g(\mathbf{r}_1, \mathbf{r}_2, t) \frac{\partial V(r_{12})}{\partial \mathbf{r}_1}. \quad (36)$$

Again, expanding $\rho(\mathbf{r}_2)$ about \mathbf{r}_1 , it is easy to see that ρ^2 corrections to the pressure tensor will be obtained. A similar result is obtained in the Enskog hard

sphere model.¹⁵ Addition corrections will result from consideration of gradient expansions of $g(\mathbf{r}_1, \mathbf{r}_2, t)(\partial V(r_{12})/\partial \mathbf{r}_1)$. Finally, long and short range contributions from the potential energy may be determined in a like fashion.

4.2. Macroscopic equations

At the continuum level, use of the BGK approximation [Eq. (31)] will obtain the following Euler equations,

$$\begin{aligned}\frac{d\rho}{dt} &= -\rho \nabla \cdot \mathbf{v} \\ \rho \frac{d\mathbf{v}}{dt} &= -\nabla \cdot \overset{\leftrightarrow}{P}^0 \\ \rho \frac{de}{dt} &= -\overset{\leftrightarrow}{P}^0 : \overset{\leftrightarrow}{\Lambda}\end{aligned}$$

where $\Lambda_{ij} = (1/2)(\partial v_i/\partial x_j) + (\partial v_j/\partial x_i)$ the internal energy, $e = (3/2)(K/m)T + (\phi/\rho)$ and the pressures tensor $\overset{\leftrightarrow}{P}^0_{ij} = nKT\delta_{ij} + B_{ij}$ is modified to include the intermolecular forces. The next order correction to the Euler equations entails solving for $\delta P_1 = P_1 - P^{eq}$ to determine corrections to the transport equations from viscous effects and thermal conductivity. At this order the additional terms in the Hermite expansion do not contribute to the viscosity, μ , and the thermal conductivity, K_t , so that the usual expressions $\mu = n\lambda KT$ and $K_t = (5/2)n\lambda K^2 T/m$ are obtained. While this result holds for the continuum case, corrections would appear in the lattice Boltzmann methods due to discretization. Finally, if needed, generalization to different Prandtl number can be obtained using the ellipsoidal Equilibrium distribution or multiple relaxation times.²⁵

5. Numerical Example

In the previous sections, several methods for the incorporation of full energy conservation in discrete Boltzmann methods were described. At this point it would be useful to illustrate these ideas with a numerical example and verify that, for example, the total energy is conserved. Here the method of rescaling the velocity and temperature (or internal energy) in a thermal equilibrium distribution in order to construct the modified BGK collision term will be utilized.

Consider the case of a low density system of particles governed by a 6-12 Lennard-Jones (LJ) interaction potential. In this low density regime we make use of the molecular chaos approximation and, for simplicity, approximate the two point correlation function, to lowest order, by $g(r) = \exp[-\beta V(r)]$ where $\beta = 1/KT$.¹⁴ It is assumed that the density varies slowly over the range the LJ interaction. It is then easy to numerically evaluate ϕ , \mathbf{Z} , and $\overset{\leftrightarrow}{B}$. Note $\overset{\leftrightarrow}{B}$ is diagonal for this case since $V(r)$ is a central potential. Once ϕ , \mathbf{Z} , and $\overset{\leftrightarrow}{B}$ are evaluated the velocity and temperature are rescaled according to Eqs. (21) and (23). The time derivative of ϕ

was numerically determined to first order using information stored from the previous time step. Although a crude approximation, it serves to illustrate the method. The details of the thermal lattice Boltzmann model are given in the appendix.

The fluid system is initialized with a small random perturbation in the density and then allowed to relax to equilibrium. To demonstrate energy conservation, the global change of potential energy $\Delta\Phi$ and change in kinetic energy, ΔKE as a function of time is shown in Fig. 1. Note the sum $\Delta\Phi + \Delta KE = 0$ to the numerical accuracy of the computer. Similar results concerning conservation of mass and momentum were obtained. For this simulation it should be noted that a significant fraction of the exchange of potential energy and kinetic energy took place over 1 to 2 mean free collision times. This result is similar to that predicted in a study of LJ fluids.²⁶

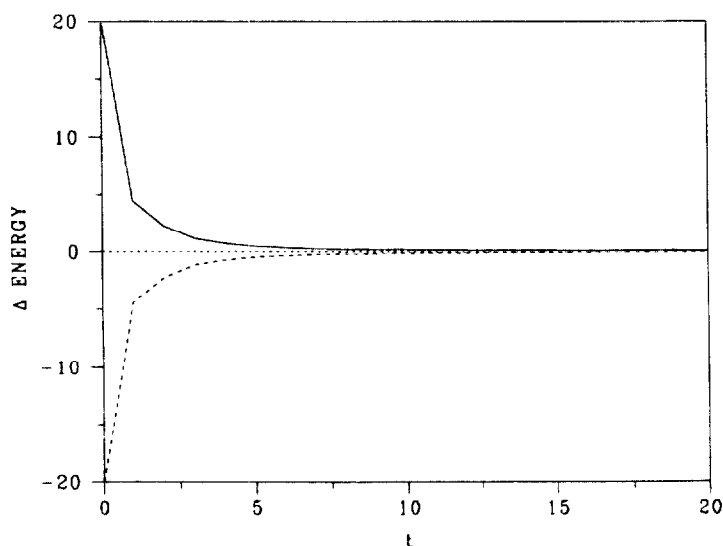


Fig. 1. The global change in potential energy and kinetic energy for a fluid system initially subject to a small density perturbation. The system size studied was 121^3 in lattice units, Δx . Energy is in units of $m(\Delta x/\Delta t)^2$ where $m = 1$ and the time step $\Delta t = 1$ for simplicity in this simulation. The solid line corresponds to the change in kinetic energy and the dashed line corresponds to the potential energy change at each time step. The sum of $\Delta\Phi$ and ΔKE (dotted line) is clearly equal to zero demonstrating the algorithm conserves energy.

It is interesting to see how introducing total energy conservation effects the time decay of a density fluctuation autocorrelation function, $G(t) = \langle \delta\rho(t)^2 \rangle$. Figure 2 shows the time decay of $G(t)$ for different Lennard-Jones interaction strengths. Here, results are presented for the case of a quasi-two dimensional system ($1024 \times 1024 \times 2$) to help reduce finite size effects. Clearly, the constraint of conserving both kinetic and potential energy slows the decay of $G(t)$. This effect diminishes over long times (and for weaker interaction strength) as the system approaches thermal

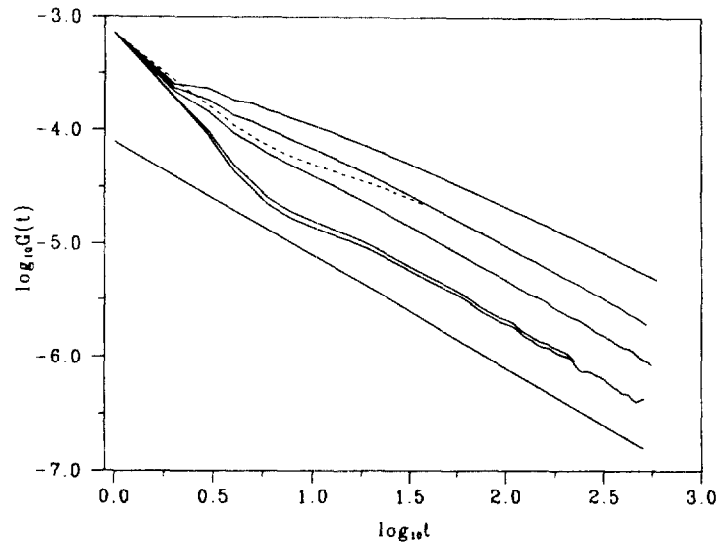


Fig. 2. The density autocorrelation function, $G(t)$, versus time, t , for a fluid system initially subject to a small density perturbation. The solid curves correspond to the fully energy conserving equation for different Lennard-Jones interaction strengths. From top to bottom the strength of interaction is 0.04, 0.03, 0.02, 0.004, and 0.0 in units of KT . The straight line has a slope of -1 to help guide the eye. The dashed line corresponds to the Shan-Chen model with interaction strength equal to 0.04.

equilibrium. The simulations carried out were consistent with $G(t) \sim t^{-1}$ at long times. Such scaling behavior is associated with the decay of the thermal diffusivity mode in the study of hydrodynamic fluctuations²⁷ which predicts $G(t) \sim t^{-D/2}$ where D is the spatial dimension.

Figure 2 also includes $G(t)$ for the case where the constraint of energy conservation is removed while still including a forcing due to the interaction potential. This case is similar to the Shan-Chen model. Comparing to the fully energy-conserving case with the same LJ interaction strength, there is a clear difference in the early rate of decay of $G(t)$ indicating that the short time behavior of this system strongly depends on whether or not one imposes energy conservation. This may be an important consideration when modeling systems that are dynamically driven and subject to frequent perturbations over time.

6. Discussion and Conclusion

To properly construct a collision operator, based on the BBGKY equations, the pair potential and two point correlation function are needed as input. Any model, whether discrete Boltzmann or CFD/free energy approaches, must at minimum make an implicit assumption about pair correlations since they are related to the equation of state, chemical potential and the transport properties of the fluid modeled.

The two point correlation function, which in turn depend on the pair potential, can be approximated by a variety of methods based on either closure of the BBGKY hierarchy or by molecular dynamics simulations. For the case of BBGKY closure, methods¹⁴ of approximating the pair correlation function such as Percus Yevick (PY) theory and the Hypernetted chain (HNC) theory work well for many low to moderate density fluids. At the lowest order approximation the equilibrium two point correlation function coupled with the molecular chaos assumption could be utilized. To go to a higher order approximation or model dense fluids, a better understanding of the nonequilibrium form of pair correlations and velocity correlations is needed. In this case, molecular dynamics may prove a valuable tool for probing the functional form of velocity correlations or other interesting behavior like the vortex motion found in hard sphere simulations.¹⁶ In addition, experimental data from neutron scattering, which can also provide information about both pair and velocity correlations, could help guide construction of the collision operator.

The methods described in this paper should be readily adaptable to existing thermal discrete Boltzmann models.¹² Rescaling the temperature via Eq. (5) without explicit reference to the potential energy ϕ may be subject to large numerical error. It may be preferable to use Eq. (8) and estimate $\partial_t \phi$ by a numerical algorithm such as predictor-corrector since ϕ can be determined at every time step.

While a few numerical tests of the above scheme have been performed in the regime of low density, demonstrating that energy was clearly conserved to the numerical accuracy of the computer, further tests are needed to examine the stability of such numerical algorithms especially near a critical temperature or for the case of a deep quench where density variations can be large. Indeed, thermal lattice Boltzmann methods are notoriously unstable.²² To better model more realistic systems with greater density or density gradients other implementations of the discrete Boltzmann method such as finite difference or volumetric methods should be considered.

It would also be interesting to examine the effect of resolution on simulations. At a coarse resolution the above system of equations should describe the time evolution of a macroscopic fluid element. At finer resolution, density variations at the atomic level could be probed although computational requirements for such studies may be prohibitive.

In summary, starting with the BBGKY formalism, the moments to be satisfied by the collision operator so that energy conservation in a discrete Boltzmann equation is rigorously maintained were presented. Several methods for constructing the collision operator based on these moment conditions were described. To illustrate the method, a simple numerical simulation was described. The decay of the density autocorrelation function was found to be consistent with the theory of hydrodynamic fluctuations. It was also shown that the isothermal nonideal gas model of Shan and Chen was recovered by this more general approach.

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Appendix: Thermal Lattice Boltzmann Model

The thermal lattice Boltzmann model used in this paper was constructed such that the lowest 26 moments of the equilibrium distribution match those of the Maxwell-Boltzmann distribution in order to obtain closure of the mass, momentum and energy equations (thermal only).^{22,23} The coefficients of the equilibrium distribution were worked out for a 4D FCHC lattice and then projected to 3D. The resulting 3D lattice vectors, \mathbf{j}_i , are all the permutations of $(\pm 1, \pm 1, 0)$, $(\pm 1, 0, 0)$, $(\pm 1, \pm 1, \pm 1)$, $(\pm 2, 0, 0)$ and $(0, 0, 0)$ where $1 \leq i \leq 12$, $13 \leq i \leq 18$, $19 \leq i \leq 26$, $27 \leq i \leq 32$, and $33 \leq i \leq 34$ respectively (note due to a degeneracy in projecting from 4D to 3D there are two rest mass particles). The equilibrium distribution was solved for to fourth order in velocity and has the following form

$$n_i^{\text{eq}} = t_i \rho (a_i + b_i \mathbf{j}_i \cdot \mathbf{v} + c_i v^2 + d_i (\mathbf{j}_i \cdot \mathbf{v})^2 + e_i (\mathbf{j}_i \cdot \mathbf{v}) v^2 + f_i (\mathbf{j}_i \cdot \mathbf{v})^3 + g_i (\mathbf{j}_i \cdot \mathbf{v})^2 v^2 + h_i v^4)$$

where the coefficients are for $1 \leq i \leq 18$, $a_i = (2e - (3/2)e^2)/24$, $b_i = (2 - (3/2)e)/12$, $c_i = ((3/2)e - 2)/24$, $d_i = (1 - e)/4$, $e_i = -1/8$, $f_i = 1/12$, $g_i = -1/16$, $h_i = 1/48$. For $19 \leq i \leq 32$, $a_i = (-e + (3/2)e^2)/48$, $b_i = (-1 + (3/2)e)/24$, $c_i = (1 - (3/2)e)/48$, $d_i = (2e - 1)/32$, $e_i = 0$, $f_i = 1/96$, $g_i = 1/64$, $h_i = -1/96$ also $n_{33}^{\text{eq}} = t_{33} \rho (a_{33} + c_{33} v^2 + h_{33} v^4)$ with $a_{33} = (-e + (3/2)e^2)/48$, $c_{33} = (1 - (3/2)e)/48$, $h_{33} = -1/96$ and $n_{34}^{\text{eq}} = t_{34} \rho (a_{34} + c_{34} v^2 + h_{34} v^4)$ with $a_{34} = (1 + (3/4)e^2 - (3/2)e)$, $c_{34} = -(3/4)(1 - e)$, $h_{34} = 1/8$. $t_i = 1$ for $1 \leq i \leq 12$, $t_i = 2$ for $12 \leq i \leq 26$, $t_i = 2$ for $19 \leq i \leq 26$. and $t_i = 1$ for $27 \leq i \leq 32$, $t_{33} = 2$, and $t_{34} = 1$.

In projection from 4D to 3D the assumption is made that there is no net flux and no gradients of any quantity in the fourth dimension. However, there is still an internal degree of freedom associated with a fourth component so that the internal energy, e , is actually given by

$$\rho e = \frac{1}{2} \sum n_i^{\text{eq}} (\mathbf{j}_i \cdot \mathbf{v})^2 + \frac{1}{2} \sum n_i^{\text{eq}} (j'_i)^2$$

where the j'_i account for contributions to the internal energy associated with a fourth dimension. For this model, $j'_i = 0$ for $1 \leq i \leq 12$, $j'_i = 1$ for $18 \leq i \leq 26$, $j'_i = 0$ for $27 \leq i \leq 32$, $j'_i = 2$ for $i = 33$, and $j'_i = 0$ for $i = 34$.

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