

Mesoscopic model for solvent dynamics

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Complex fluids such as polymers in solution or multispecies reacting systems in fluid flows often can be studied only by employing a simplified description of the solvent motions. A stochastic model utilizing a synchronous, discrete-time dynamics with continuous velocities and local multiparticle collisions is developed for this purpose. An H theorem is established for the model and the hydrodynamic equations and transport coefficients are derived. The results of simulations are presented which verify the properties of the model and demonstrate its utility as a hydrodynamics medium for the study of complex fluids. © 1999 American Institute of Physics.

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I. INTRODUCTION

The investigation of the dynamics of complex fluids is a challenging task. In complex chemically reacting systems many chemical species dissolved in a solvent may undergo sequences of reactions leading to oscillations or chemical patterns.¹ The reactive dynamics may depend on the solvent motions since the fluid flow fields influence the nature of the mixing of the species. Specific instabilities have been ascribed to flow effects, such as differential-flow-induced chemical instabilities.² Reactions in porous media constitute another example. Here one is interested in how a flow field in a complicated medium influences the reactions that may themselves change the nature of the medium, for instance, through dissolution reactions.³ Similar considerations apply to the study of rheological properties of colloidal suspensions or polymers in solution.⁴ An especially important class of problems concerns the conformational dynamics of biopolymers such as proteins in solution.⁵

All of the above examples, and others like them, share the feature that one is interested in the detailed microscopic dynamics of some degrees of freedom of the system interacting with a solvent whose dynamics is essential for the phenomena but whose detailed properties are not of interest. The systems are sufficiently complex that a full molecular dynamics (MD) simulation of the system plus solvent is impossible. Furthermore, the dynamics of interest often occurs on long time scales and over long distances; for example, the relaxation times for large polymers can be very long and the distance scales for many chemical pattern forming processes range from mesoscopic to macroscopic scales.

In such circumstances one is led to consider mesoscopic models for the solvent dynamics that incorporate the essential dynamical properties, yet are simple enough to be simulated for long times and on long distance scales.⁶ These mesoscopic models must not only faithfully reproduce the main dynamical features of the solvent but must also be microscopic in character to permit coupling between microscopic

degrees of freedom, whose dynamics are of interest, and the solvent. For instance, one must be able to couple the monomer units of a polymer to the solvent or the reactive collisions between molecules to the flow of the solvent responsible for their mixing.

A variety of mesoscopic models have been constructed for this purpose ranging from Langevin models that have been employed as simple “heat baths” in MD studies of biomolecule dynamics,⁷ to schemes such as Direct Simulation Monte Carlo (DSMC) methods,⁸ lattice Boltzmann methods,⁹ and extensions of hydrodynamic lattice gas automaton models.¹⁰

In this paper we present a mesoscopic model for simulating a fluid that has the desirable features mentioned above. The fluid is modeled by “particles” whose positions and velocities are treated as continuous variables. The system is coarse grained onto the cells of a regular lattice and there is no restriction on the number of particles that may reside in a cell. The dynamics is carried out synchronously at discrete time steps. Particle streaming is treated exactly while the cells are the collision volumes for a multiparticle collision dynamics that differs from that of DSMC schemes. The dynamics satisfies the mass, momentum and energy conservation laws and we shall show it yields the correct hydrodynamic equations. Since it is a particle model, collisional coupling to other microscopic degrees of freedom is easily incorporated and its application to complex system geometries is straightforward.

The outline of the paper is as follows. Section II describes the streaming and multiparticle collision dynamics that forms the basis of the mesoscale description of the system. The Boltzmann approximation to the full dynamics is considered in Sec. III; a Boltzmann-type kinetic equation is derived, an H theorem for the evolution is proved and the Chapman–Enskog expansion is used to derive the Navier–Stokes equations and determine the transport coefficients for a particular collision model. In Sec. IV simulations are carried out to confirm the utility of the model. The velocity

distribution is shown to be Maxwellian and the hydrodynamic flow patterns for flow past a disk are examined. The conclusions of the study are presented in Sec. V.

II. STREAMING AND MULTIPARTICLE COLLISION DYNAMICS

The system we study consists of N particles of unit mass with position \mathbf{x}_i and velocity \mathbf{v}_i coordinates, $i=1,2,\dots,N$. The evolution through a unit time interval is given by successive application of streaming and collision steps. During the streaming step the particle positions change in the standard way,¹¹

$$\mathbf{x}_i \rightarrow \mathbf{x}_i + \mathbf{v}_i, \quad (1)$$

while in the collision step particle velocities transform according to

$$\mathbf{v}_i \rightarrow \mathbf{V} + \hat{\omega}[\mathbf{v}_i - \mathbf{V}], \quad (2)$$

where $\hat{\omega}$ is a random rotation from a set Ω and \mathbf{V} is the average velocity of the colliding particles. In this multiparticle collision event, the velocity vector of particle i , relative to the mean velocity \mathbf{V} , is rotated by a randomly chosen rotation operator to give the post-collision value of the velocity. We shall show below that the mass, momentum and energy collision invariants are preserved under this multiparticle collision dynamics.

We imagine coarse graining the system into Wigner–Seitz cells centered on the nodes of a regular lattice L . For a cubic lattice the Wigner–Seitz cell \mathcal{V} is defined by $|\mathbf{x} - \boldsymbol{\xi}| < 1/2$, where we introduce the norm $|\mathbf{x}| = \max(x_x, x_y, x_z)$ and $\boldsymbol{\xi}$ denotes a lattice coordinate. These cells define the collision volumes for the multiparticle collision dynamics. The collisions are simultaneously performed on all particles in a Wigner–Seitz cell with the same rotation $\hat{\omega}$, but $\hat{\omega}$ may differ from cell to cell.

The evolution governed by Eqs. (1) and (2) may be written in the form of a Liouville equation for the probability density,

$$P(\mathbf{V}^{(N)}, \mathbf{X}^{(N)} + \mathbf{V}^{(N)}, t+1) = \mathcal{C}P(\mathbf{V}^{(N)}, \mathbf{X}^{(N)}, t), \quad (3)$$

where

$$\begin{aligned} \mathcal{C}P(\mathbf{V}^{(N)}, \mathbf{X}^{(N)}, t) &= \frac{1}{\|\Omega\|^L} \sum_{\Omega^L} \int d\check{\mathbf{V}}^{(N)} P(\check{\mathbf{V}}^{(N)}, \mathbf{X}^{(N)}, t) \\ &\times \prod_{i=1}^N \delta(\mathbf{v}_i - \mathbf{V}_{\boldsymbol{\xi}} - \hat{\omega}_{\boldsymbol{\xi}}[\check{\mathbf{v}}_i - \mathbf{V}_{\boldsymbol{\xi}}]), \end{aligned} \quad (4)$$

where $\mathbf{X}^{(N)} = (\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$, $\mathbf{V}^{(N)} = (\mathbf{v}_1, \mathbf{v}_2, \dots, \mathbf{v}_N)$, $\check{\mathbf{V}}^{(N)} = (\check{\mathbf{v}}_1, \check{\mathbf{v}}_2, \dots, \check{\mathbf{v}}_N)$ and, $L = \|L\|$ is the number of lattice nodes.

The evolution described by Eqs. (1) and (2) preserves total energy and momentum of the particles in each cell, as can be seen from the identities,

$$\sum_{i \in \mathcal{V}} \mathbf{v}_i = \sum_{i \in \mathcal{V}} (\mathbf{V} + \hat{\omega}[\mathbf{v}_i - \mathbf{V}])$$

and

$$\sum_{i \in \mathcal{V}} \|\mathbf{v}_i\|^2 = \sum_{i \in \mathcal{V}} \|\mathbf{V} + \hat{\omega}[\mathbf{v}_i - \mathbf{V}]\|^2. \quad (5)$$

We note that the elementary measure $d\Gamma = \prod d\mathbf{x}_i d\mathbf{v}_i$ is invariant with respect to streaming and collision transformations. For the (deterministic) streaming operator it follows from the identity,

$$\text{Jacobian} \left(\frac{\partial \mathbf{x}_i(t+1)}{\partial \mathbf{x}_i(t)} \right) = \mathbf{1}, \quad (6)$$

and for the collision transformation it results from the semi-detailed balance condition and phase space volume conservation during rotations,

$$\begin{aligned} \prod_i d\mathbf{v}_i &= \sum_{\hat{\omega}, \check{\mathbf{V}}^{(N)} | \hat{\omega}(\check{\mathbf{V}}^{(N)}) = \mathbf{V}^{(N)}} p(\hat{\omega} | \check{\mathbf{V}}^{(N)}) \prod_i d\check{\mathbf{v}}_i \\ &= \prod_i d\mathbf{v}_i \sum_{\hat{\omega}, \check{\mathbf{V}}^{(N)} | \hat{\omega}(\check{\mathbf{V}}^{(N)}) = \mathbf{V}^{(N)}} p(\hat{\omega} | \check{\mathbf{V}}^{(N)}), \end{aligned} \quad (7)$$

which is valid if the choice of the rotations is independent of velocities. Here $p(\hat{\omega} | \check{\mathbf{V}}^{(N)})$ is the conditional probability of the rotation $\hat{\omega}$ given $\check{\mathbf{V}}^{(N)}$. In the above equation \mathbf{v}_i and $\check{\mathbf{v}}_i$ are the post- and precollision velocities, respectively. Assuming the validity of the ergodic hypothesis, which is supported by the results of numerical simulations, we conclude that the stationary distribution is given by the microcanonical ensemble expression,

$$\begin{aligned} P(\mathbf{V}^{(N)}, \mathbf{X}^{(N)}) &= A \delta \left(\frac{\beta}{2N} \sum_{i=1}^N \|\mathbf{v}_i\|^2 - \frac{d}{2} \right) \\ &\times \delta \left(\sum_{i=1}^N [\mathbf{v}_i - \mathbf{u}] \right), \end{aligned} \quad (8)$$

where \mathbf{u} is the mean velocity of the system. After integration over the coordinates and velocities of particles with $i=2, \dots, N$ we arrive in the limit of large N at the Maxwell distribution,

$$P_m(\mathbf{v}_1, \mathbf{x}_1) = \frac{1}{V} \left(\frac{\beta}{2\pi} \right)^{d/2} \exp(-\beta \|\mathbf{v}_1 - \mathbf{u}\|^2/2), \quad (9)$$

where $\beta = (1/k_B T)$, V is the system volume and d is the dimension. Although the correct distribution results from the semidetailed balance condition, the computation of the transport coefficients is greatly simplified if we impose detailed balance conditions on the collision operator. In the current context this is tantamount to $\Omega = \Omega^{-1}$.

III. BOLTZMANN APPROXIMATION

In Sec. II we found that the stationary distribution for the one-particle velocity distribution was Maxwellian. In order to study the relaxation to equilibrium we assume that there are no correlations among the colliding particles in Eq. (3). In this case the probability distribution P is a product of identical one-particle probability distributions,

$$P(\mathbf{V}^{(N)}, \mathbf{X}^{(N)}, t) = \prod_{i=1}^N P_1(\mathbf{v}_i, \mathbf{x}_i, t). \quad (10)$$

In order to derive the Boltzmann equation we multiply Eq. (3) by $\sum_i \delta(\mathbf{v}-\mathbf{v}_i) \delta(\mathbf{x}-\mathbf{x}_i)$ and subsequently integrate over \mathbf{v}_i and \mathbf{x}_i , where $i=1, \dots, N$. Focusing on \mathbf{x} in cell ξ and accounting for all possible ways of assigning n particles to the cell, we obtain

$$\begin{aligned} \mathcal{C}(f(t)) &= \sum_{n=1}^N \binom{N}{n} \left[\int \prod_{i=n+1}^N d\mathbf{x}_i d\check{\mathbf{v}}_i P_1(\check{\mathbf{v}}_i, \mathbf{x}_i, t) \right. \\ &\quad \times (\theta(|\mathbf{x}_i - \xi| - 1/2)) \times \int_{\mathcal{V}^n} d\check{\mathbf{V}}^{(n)} d\mathbf{X}^{(n)} \\ &\quad \left. \times \left[\prod_{i=1}^n d\mathbf{x}_i d\check{\mathbf{v}}_i P_1(\check{\mathbf{v}}_i, \mathbf{x}_i, t) \right] \Delta(\mathbf{v}, \check{\mathbf{V}}^{(n)}), \right. \end{aligned} \quad (11)$$

where

$$\Delta(\mathbf{v}, \check{\mathbf{V}}^{(n)}) = \frac{1}{\|\Omega\|} \sum_{i, \hat{\omega} \in \Omega} \delta(\mathbf{v} - \mathbf{V} + \hat{\omega}[V - \check{v}_i]) \delta(\mathbf{x} - \mathbf{x}_i). \quad (12)$$

In writing this equation we have used the fact that we may express $P_1(\mathbf{v}_i, \mathbf{x}_i, t)$ as the sum of two terms,

$$\begin{aligned} P_1(\mathbf{v}_i, \mathbf{x}_i, t) &= P_1(\mathbf{v}_i, \mathbf{x}_i, t) (\theta(|\mathbf{x}_i - \xi| - 1/2) \\ &\quad + \theta(1/2 - |\mathbf{x}_i - \xi|)), \end{aligned} \quad (13)$$

where θ is the Heaviside function. Particles with coordinates outside the cell do not contribute to the collision term and this is accounted for by the Heaviside function in the first factor of Eq. (11). We use the fact that the prefactor in Eq. (11) may be written as

$$\begin{aligned} &\int \dots \int \prod_{i=n+1}^N d\mathbf{x}_i d\check{\mathbf{v}}_i P_1(\check{\mathbf{v}}_i, \mathbf{x}_i, t) (\theta(|\mathbf{x}_i - \xi| - 1/2)) \\ &= \left[\int d\mathbf{x}_i d\check{\mathbf{v}}_i P_1(\check{\mathbf{v}}_i, \mathbf{x}_i, t) (\theta(|\mathbf{x}_i - \xi| - 1/2)) \right]^{N-n} \\ &= \left(1 - \frac{\rho_\xi}{N} \right)^{N-n}, \end{aligned} \quad (14)$$

where ρ_ξ is the total particle number density in the Wigner-Seitz cell ξ . In the large N limit we have $\binom{N}{n} (1 - (\rho_\xi/N))^{N-n} \approx (N^n/n!) e^{-\rho_\xi}$. Incorporating the factor of N into the definition $f(\mathbf{v}, \mathbf{x}, t) = NP_1(\mathbf{v}, \mathbf{x}, t)$, we obtain the Boltzmann equation,

$$f(\mathbf{v}, \mathbf{x} + \mathbf{v}, t + 1) = \mathcal{C}(f(t)), \quad (15)$$

where

$$\mathcal{C}(f(t)) = \sum_{n=1}^{\infty} \frac{e^{-\rho_\xi}}{n!} \int_{\mathcal{V}^n} d\check{\mathbf{V}}^{(n)} d\mathbf{X}^{(n)} F(\check{\mathbf{V}}^{(n)}, \mathbf{X}^{(n)}, t) \Delta(\mathbf{v}, \check{\mathbf{V}}^{(n)}), \quad (16)$$

and we have defined

$$F(\check{\mathbf{V}}^{(n)}, \mathbf{X}^{(n)}, t) = \prod_{i=1}^n f(\check{\mathbf{v}}_i, \mathbf{x}_i, t). \quad (17)$$

The prefactor in Eq. (16) shows that the cell particle number is Poisson distributed.

Equation (15) preserves expectation values of integrals of motion such as the density, momentum and energy. Denoting these quantities by $\mathcal{J}^1(\mathbf{v}) = 1$, $\mathcal{J}^2(\mathbf{v}) = \mathbf{v}$, and $\mathcal{J}^3(\mathbf{v}) = \frac{1}{2}\|\mathbf{v}\|^2$, respectively, we have

$$\begin{aligned} &\int d\mathbf{v} d\mathbf{x} \mathcal{J}^\alpha(\mathbf{v}) f(\mathbf{v}, \mathbf{x}, t + 1) \\ &= \int d\mathbf{v} d\mathbf{x} \mathcal{J}^\alpha(\mathbf{v}) \mathcal{C}(f(t)) \\ &= \sum_{i, \xi, n=1}^{\infty} \frac{e^{-\rho_\xi}}{n!} \int_{\mathcal{V}^n} d\check{\mathbf{V}}^{(n)} d\mathbf{X}^{(n)} \mathcal{J}^\alpha(\check{\mathbf{v}}_i) F(\check{\mathbf{V}}^{(n)}, \mathbf{X}^{(n)}, t) \\ &= \int d\mathbf{v} d\mathbf{x} \mathcal{J}^\alpha(\mathbf{v}) f(\mathbf{v}, \mathbf{x}, t), \end{aligned} \quad (18)$$

where we used the following identities:

$$\sum_i 1 = \sum_i 1, \quad (19a)$$

$$\sum_i (V - \hat{\omega}[V - \check{v}_i]) = \sum_i \check{v}_i, \quad (19b)$$

$$\sum_i \|V - \hat{\omega}[V - \check{v}_i]\|^2 = \sum_i \|\check{v}_i\|^2, \quad (19c)$$

for the density, momentum, and energy conservation laws, respectively.

A. H theorem

The evolution Eq. (3) involves a multiparticle collision term and it not immediately clear that an H theorem exists.

We define the H functional in terms of the reduced one-particle distribution function,

$$\begin{aligned} H(t) &= \int d\mathbf{v} d\mathbf{x} f(\mathbf{v}, \mathbf{x}, t) \ln f(\mathbf{v}, \mathbf{x}, t) \\ &= \sum_{\xi, n \in \mathbb{N}} \frac{e^{-\rho_\xi}}{n!} \int_{\mathcal{V}^n} d\mathbf{V}^{(n)} d\mathbf{X}^{(n)} \prod_{i=1}^n f(\mathbf{v}_i, \mathbf{x}_i, t) \ln \\ &\quad \times \prod_{i=1}^n f(\mathbf{v}_i, \mathbf{x}_i, t), \end{aligned} \quad (20)$$

where the second equality arises from the representation of the system in terms of phase space cells and makes use of the resolution of identity $1 = \sum_{n \geq 0} (e^{-x} x^n / n!)$. In the Appendix we show that $H(t)$ decreases on each evolution step so that

$$H(t) \geq \int d\check{\mathbf{v}} d\mathbf{x} f(\check{\mathbf{v}}, \mathbf{x}, t + 1) \ln f(\check{\mathbf{v}}, \mathbf{x}, t + 1). \quad (21)$$

For the fixed momentum and energy expectation values the Maxwell distribution,

$$f_m = \frac{N}{V} \left(\frac{1}{2\pi k_B T} \right)^{d/2} e^{-\frac{\|\mathbf{v}-\mathbf{u}\|^2}{2k_B T}}, \quad (22)$$

provides a lower bound to the H functional. This follows from the identity,

$$\int d\mathbf{x}d\mathbf{v}f(\mathbf{v},\mathbf{x})\ln f_m(\mathbf{v}) = \int d\mathbf{x}d\mathbf{v}f_m(\mathbf{v})\ln f_m(\mathbf{v}), \quad (23)$$

and the inequality,

$$\begin{aligned} & \int d\mathbf{x}d\mathbf{v}f(\mathbf{v},\mathbf{x})\ln \frac{f(\mathbf{v},\mathbf{x})}{f_m(\mathbf{v})} \\ &= N \int d\mathbf{x}d\mathbf{v} \frac{f_m(\mathbf{v})}{N} \frac{f(\mathbf{v},\mathbf{x})}{f_m(\mathbf{v})} \ln \frac{f(\mathbf{v},\mathbf{x})}{f_m(\mathbf{v})} \geq 0. \end{aligned} \quad (24)$$

Equations (18) show that the expectation values of the density, momentum and energy are conserved during evolution under the Boltzmann equation; thus, completing the proof of the H theorem.

B. Chapman–Enskog asymptotic expansion

We derive hydrodynamical equations by using an expansion of the reduced probability distribution in slowly varying density fields. This Chapman–Enskog procedure^{12,13} is based on the assumption that any relevant functional can be expanded into a series of partial derivatives of the conserved fields. After scaling $\mathbf{x} \rightarrow \varepsilon \mathbf{x}$ and $t \rightarrow \varepsilon t$ the expansion is ordered in powers of ε .

We rewrite Eq. (15) in terms of the average cell probability distribution \bar{f} and averaged collision operator $\bar{\mathcal{C}}$,

$$\bar{f}(\mathbf{v}, \boldsymbol{\xi}, t) = \int_{|\mathbf{x}-\boldsymbol{\xi}| < 1/2} d\mathbf{x}f(\mathbf{v}, \mathbf{x}, t), \quad (25)$$

$$\bar{\mathcal{C}}(\bar{f}) = \int_{|\mathbf{x}-\boldsymbol{\xi}| < 1/2} d\mathbf{x}\mathcal{C}(f). \quad (26)$$

If f is a smooth function the following relation holds

$$\int_{|\mathbf{x}-\boldsymbol{\xi}| < 1/2} d\mathbf{x}e^{\partial_t + \mathbf{v} \cdot \nabla} f(\mathbf{v}, \mathbf{x}, t) = e^{\partial_t + \mathbf{v} \cdot \nabla} \bar{f}(\mathbf{v}, \boldsymbol{\xi}, t), \quad (27)$$

and the evolution of the averaged cell probability distribution is described by a Galilean invariant, spherically isotropic equation

$$e^{\partial_t + \mathbf{v} \cdot \nabla} \bar{\mathcal{C}}\bar{f} = \bar{\mathcal{C}}(\bar{f}). \quad (28)$$

It is further assumed that the reduced probability distribution function \bar{f} is defined by the instantaneous spatial distribution of local collision invariants \mathcal{J}^α ,

$$\bar{f}(\mathbf{v}, \boldsymbol{\xi}, t) = \bar{f}(\mathbf{v}, \boldsymbol{\rho}(\boldsymbol{\xi}, t)) = \sum_{n \geq 0} \varepsilon^n \bar{f}_n(\mathbf{v}, \boldsymbol{\rho}(\boldsymbol{\xi}, t)). \quad (29)$$

The density of a local collision invariant is given by the average value

$$\boldsymbol{\rho}(\boldsymbol{\xi}, t) = \int d\mathbf{v} \mathcal{J} \bar{f}(\boldsymbol{\xi}, \mathbf{v}, t) = \langle \mathcal{J} \bar{f}(\boldsymbol{\xi}, \mathbf{v}, t) \rangle, \quad (30)$$

and to ensure uniqueness an additional requirement is imposed,

$$\langle \mathcal{J}^\alpha \bar{f}_n(\boldsymbol{\xi}, \mathbf{v}, t) \rangle = 0 \text{ for all } \alpha \text{ and } n > 0, \quad (31)$$

where \mathcal{J} is the set of the density, momentum, and energy dynamical variables introduced earlier.

Time evolution of a functional of the conserved quantities is governed by an operator given as an expansion in the small parameter ε ,

$$\frac{\partial}{\partial t} = \sum_{n \geq 0} \varepsilon^n \mathcal{D}_n, \quad (32)$$

and the gradient term in Eq. (28) is scaled by ε . The expansion of the collision operator in a series in ε is written formally as

$$\bar{\mathcal{C}}(\bar{f}) = \sum_{n \geq 0} \varepsilon^n \bar{\mathcal{C}}_n(\bar{f}). \quad (33)$$

To ensure the identity $\langle \mathcal{J} \bar{\mathcal{C}}(\bar{f}) \rangle = \langle \mathcal{J} \bar{f} \rangle$ we constrain the average of each term of the series by $\langle \mathcal{J} \bar{\mathcal{C}}_n(\bar{f}) \rangle = \langle \mathcal{J} \bar{f}_n \rangle$.

By expanding the evolution Eq. (28) in powers of ε we arrive at the following set of equations:

$$\bar{\mathcal{C}}_0(\bar{f}) = \bar{\mathcal{C}}(\bar{f}_0) = \bar{f}_0, \quad (34a)$$

$$\bar{\mathcal{C}}_1(\bar{f}) = \bar{f}_1 + [\mathcal{D}_0 + \mathbf{v} \cdot \nabla_{\boldsymbol{\xi}}] \bar{f}_0, \quad (34b)$$

$$\bar{\mathcal{C}}_2(\bar{f}) = \bar{f}_2 + \mathcal{D}_1 \bar{f}_0 + [\mathcal{D}_0 + \mathbf{v} \cdot \nabla_{\boldsymbol{\xi}}] \bar{f}_1 + \frac{1}{2} [\mathcal{D}_0 + \mathbf{v} \cdot \nabla_{\boldsymbol{\xi}}]^2 \bar{f}_0. \quad (34c)$$

The solution of Eq. (34a) yields a local Maxwellian distribution,

$$\bar{f}_0 = \rho \left(\frac{1}{2\pi k_B T} \right)^{d/2} e^{-\langle \|\mathbf{v}-\mathbf{u}\|^2 / 2k_B T \rangle}. \quad (35)$$

The average of the local collision invariants over \mathbf{v} commutes with the operator \mathcal{D}_i so that integration of Eq. (34b) yields

$$\mathcal{D}_0 \rho^\alpha = -\nabla_{\boldsymbol{\xi}} \cdot \langle \mathcal{J}^\alpha \mathbf{v} \bar{f}_0 \rangle. \quad (36)$$

The average of Eq. (34c) gives the second order correction to the Euler equations,

$$\mathcal{D}_1 \rho^\alpha = -\frac{1}{2} \langle \mathcal{J}^\alpha [\mathcal{D}_0 + \nabla_{\boldsymbol{\xi}} \cdot \mathbf{v}] (\bar{f}_1 + \bar{\mathcal{C}}_1(\bar{f})) \rangle,$$

and after transformations (Euler equations are dissipationless),

$$\mathcal{D}_1 \rho^\alpha = -\frac{1}{2} \nabla_{\boldsymbol{\xi}} \cdot \langle \mathcal{J}^\alpha \mathbf{v} (\bar{f}_1 + \bar{\mathcal{C}}_1(\bar{f})) \rangle, \quad (37)$$

where we used the conditions on $\langle \mathcal{J}^\alpha \bar{f}_1 \rangle$ and $\langle \mathcal{J}^\alpha \bar{\mathcal{C}}_1(\bar{f}) \rangle$.

C. Navier–Stokes equation

In this section we apply general formulas (34a)–(34c) to a specific collision model. Regardless of the collision model, the equation for the zeroth expansion term has the same form and constitutes the Euler equations of compressible flow. Evaluation of the averages in Eq. (36) yields the following results for the evolution of the conserved quantities:

$$\partial_t \rho + \nabla_{\beta} \rho u_{\beta} = 0,$$

$$\partial_t \rho u_{\alpha} + \nabla_{\beta} \rho u_{\beta} u_{\alpha} + k_B \nabla_{\alpha} \rho T = 0, \quad (38)$$

$$\partial_t \left[\frac{1}{2} \rho \|\mathbf{u}\|^2 + C_v \rho T \right] + \nabla_{\beta} \rho u_{\beta} \left[\frac{1}{2} \rho \|\mathbf{u}\|^2 + C_p \rho T \right] = 0,$$

where $C_v = dk_B/2$ and $C_p = C_v + k_B$. The subscripts α and β refer to the Cartesian coordinates and the Einstein summa-

tion convention is used. We have dropped the subscript ξ to avoid proliferation of notation. Algebraic manipulations transform the above system into a set of evolution equations for ρ, \mathbf{v} , and T ,

$$\partial_t \rho + \nabla_\beta \rho u_\beta = 0, \tag{39a}$$

$$\partial_t u_\alpha + u_\beta \nabla_\beta u_\alpha + \frac{k_B}{\rho} \nabla_\alpha \rho T = 0, \tag{39b}$$

$$C_v [\partial_t T + u_\beta \nabla_\beta T] + k_B T \nabla_\beta u_\beta = 0. \tag{39c}$$

With the use of Eqs. (39a)–(39c) we rewrite Eq. (34b) in the following form:

$$\begin{aligned} \bar{\mathcal{C}}_1(\bar{f}) - \bar{f}_1 = \bar{f}_0 & \left(\frac{\partial \log(\bar{f}_0)}{\partial \rho} [\nabla_\beta v_\beta \rho - \nabla_\beta u_\beta \rho] + \frac{\partial \log(\bar{f}_0)}{\partial u_\beta} \right. \\ & \times \left[\nabla_\alpha v_\alpha u_\beta - u_\alpha \nabla_\alpha u_\beta - \frac{k_B}{\rho} \nabla_\beta \rho T \right] \\ & \left. + \frac{\partial \log(\bar{f}_0)}{\partial T} \left[\nabla_\beta v_\beta T - u_\beta \nabla_\beta T - \frac{k_B}{C_v} T \nabla_\beta u_\beta \right] \right). \end{aligned}$$

We substitute the explicit form of \bar{f}_0 given by Eq. (35) and, after algebraic transformation, arrive at the following equation:

$$\begin{aligned} \bar{\mathcal{C}}_1(\bar{f}) - \bar{f}_1 = \bar{f}_0 & \left(\left[\frac{\|\mathbf{c}\|^2}{2k_B T} - \frac{C_p}{k_B} \right] c_\beta \nabla_\beta \log T \right. \\ & \left. + \frac{1}{k_B T} \left[c_\beta c_\alpha - \frac{1}{d} \|\mathbf{c}\|^2 \delta_{\beta\alpha} \right] \nabla_\alpha u_\beta \right), \tag{40} \end{aligned}$$

where $\mathbf{c} = \mathbf{v} - \mathbf{u}$.

We define the function h_1 by the relation $h_1 \bar{f}_0 = \bar{f}_1$. The collision operator $\bar{\mathcal{C}}_1$ has the following form:

$$\begin{aligned} \bar{\mathcal{C}}_1(\bar{f})(\mathbf{v}) = \sum_{n=1}^{\infty} \frac{\rho^n}{n!} e^{-\rho} \int d\mathbf{V}^n \sum_{j=1}^n \delta(\mathbf{v} - \mathbf{v}_j) \int d\check{\mathbf{V}}^{(n)} R^{(n)} \\ \times (\mathbf{V}^{(n)}, \check{\mathbf{V}}^{(n)}) P_m(\check{\mathbf{V}}^{(n)}) \sum_{i=1}^n h_1(\check{\mathbf{v}}_i), \tag{41} \end{aligned}$$

where $R^{(n)}$ is defined by Eq. (A2). Using the invariance of the Maxwell distribution with respect to the collision transformation we obtain the following relation:

$$\begin{aligned} \bar{\mathcal{C}}_1(\bar{f})(\mathbf{v}) = \sum_{\omega \in \Omega, n=1}^{\infty} \frac{\rho^n}{|\Omega| n!} e^{-\rho} \int d\mathbf{V}^{(n)} \\ \times \sum_{j=1}^n \delta(\mathbf{v} - \mathbf{v}_j) P_m(\mathbf{V}^{(n)}) \sum_{i=1}^n h_1(\check{\mathbf{v}}_i), \tag{42} \end{aligned}$$

where $\check{\mathbf{v}}_i = \mathbf{V} + \hat{\omega}[\mathbf{v}_i - \mathbf{V}]$.

Equations (42) and (40) constitute a linear integral equation for h_1 , which can be split into two equations, one that involves terms $\nabla \log T$ and the other that depends on gradients of velocity fields.

Explicit calculations for two dimensions. For $d=2$ and $\Omega = \{\pi/2, -\pi/2\}$ we may show that the functions,

$$s_1 = \left[c_\alpha c_\beta - \frac{1}{d} \|\mathbf{c}\|^2 \delta_{\alpha\beta} \right] \text{ and } s_2 = \left[\frac{\|\mathbf{c}\|^2}{2T} - C_p \right] c_\alpha,$$

are eigenfunctions of the collision operator and through their eigenvalues we evaluate values of the viscosity and thermal conductivity coefficients, respectively.

Consider s_1 . Using Galilean invariance of the Boltzmann equation, without loss of generality we can choose a stationary frame with $\mathbf{u} = 0$. In this case $\mathbf{c} = \mathbf{v}$ and write

$$\begin{aligned} \frac{1}{|\Omega|} \sum_{\omega, i=1}^n h_1(\check{\mathbf{v}}_i) = \frac{1}{|\Omega|} \sum_{\omega, i=1}^n \left[\mathbf{V}_\alpha \mathbf{V}_\beta - \hat{\omega} \mathbf{V}_\alpha \hat{\omega} \mathbf{V}_\beta \right. \\ \left. + \hat{\omega} \mathbf{v}_i |_\alpha \hat{\omega} \mathbf{v}_i |_\beta - \frac{1}{2} \|\mathbf{v}_i\|^2 \delta_{\alpha\beta} \right]. \tag{43} \end{aligned}$$

By using the relations $\hat{\omega} \mathbf{v}_i |_x \hat{\omega} \mathbf{v}_i |_y = -\mathbf{v}_x \mathbf{v}_y$ and $(\hat{\omega} \mathbf{v}_i |_x)^2 = (\mathbf{v}_y)^2$ valid for $\hat{\omega} = \pm \pi/2$ we arrive at the following equation:

$$\begin{aligned} \frac{1}{|\Omega|} \sum_{\omega, i=1}^n h_1(\check{\mathbf{v}}_i) = \sum_{i=1}^n \left[2\mathbf{V}_\alpha \mathbf{V}_\beta - \|\mathbf{V}\|^2 \delta_{\alpha\beta} \right. \\ \left. - \left(\mathbf{v}_i \alpha \mathbf{v}_i \beta - \frac{1}{2} \|\mathbf{v}_i\|^2 \delta_{\alpha\beta} \right) \right]. \tag{44} \end{aligned}$$

We note that the cross terms with different particle index i vanish upon integration so that we have the following expression for the eigenvalue problem:

$$\begin{aligned} \bar{\mathcal{C}}_1(s_1 \bar{f}_0) = s_1 \bar{f}_0 \sum_{n=1}^{\infty} \frac{\rho^{n-1}}{n!} e^{-\rho} (2-n) \\ = \frac{2(1 - e^{-\rho} - \rho)}{\rho} s_1 \bar{f}_0 \equiv r_\eta s_1 \bar{f}_0. \tag{45} \end{aligned}$$

An analogous calculation for s_2 yields,

$$\bar{\mathcal{C}}_1(s_2 \bar{f}_0) = \frac{e^{-\rho} - 1}{\rho} s_2 \bar{f}_0 \equiv r_\lambda s_2 \bar{f}_0. \tag{46}$$

Using these results in Eq. (37) we may compute the shear viscosity and thermal conductivity coefficients in terms of the damping factors r_η and r_λ as,

$$\eta = \rho k_B T \frac{1 + r_\eta}{2(1 - r_\eta)} = \rho k_B T \frac{1 - e^{-\rho}}{2(e^{-\rho} - 1 + \rho)}, \tag{47}$$

and

$$\lambda = \rho k_B T \frac{1 + r_\lambda}{1 - r_\lambda} = \rho k_B T \frac{\rho - 1 + e^{-\rho}}{1 + \rho - e^{-\rho}}. \tag{48}$$

Evaluation of the averages in Eq. (37) yields the following expressions for the second order terms in the Chapman–Enskog expansion:

$$\mathcal{D}_1 \rho = 0, \tag{49}$$

$$\mathcal{D}_1 \rho u_\beta = -\nabla_\alpha \pi_{\beta\alpha}, \tag{50}$$

$$\mathcal{D}_1 \left[\frac{1}{2} \rho \|\mathbf{u}\|^2 + C_v \rho T \right] = -\nabla_\beta u_\alpha \pi_{\beta\alpha} - \nabla_\beta q_\beta, \tag{51}$$

where λ is thermal conductivity coefficient and the irreversible contribution to the pressure tensor and the heat flux are given by the following expressions:

$$\pi_{\beta\alpha} = -\eta(\nabla_{\beta}u_{\alpha} + \nabla_{\alpha}u_{\beta} - \frac{1}{2}\delta_{\beta\alpha}\nabla_{\gamma}u_{\gamma}), \quad (52)$$

$$q_{\beta} = -\lambda\nabla_{\beta}T. \quad (53)$$

In the ρ, \mathbf{u}, T set of variables the resulting hydrodynamic equations have the following standard form:

$$\partial_t\rho + \nabla_{\beta}\rho u_{\beta} = 0, \quad (54a)$$

$$\partial_t u_{\alpha} + u_{\beta}\nabla_{\beta}u_{\alpha} + \frac{1}{\rho}\nabla_{\alpha}\rho T = -\frac{1}{\rho}\nabla_{\alpha}\pi_{\beta\alpha}, \quad (54b)$$

$$C_v[\partial_t T + u_{\beta}\nabla_{\beta}T] + k_B T \nabla_{\beta}u_{\beta} = -\frac{1}{\rho}\pi_{\beta\alpha}\nabla_{\alpha}u_{\beta} - \frac{1}{\rho}\nabla_{\beta}q_{\beta}. \quad (54c)$$

Similar calculations can be carried for other collision model. For example, in three dimensions, averaging the set of all random rotations Ω yields,

$$\frac{1}{|\Omega|} \sum_{\hat{\omega}, i=1}^n h_1(\hat{\mathbf{v}}_i) = \sum_{i=1}^n \left[\mathbf{V}_{\alpha}\mathbf{V}_{\beta} - \frac{1}{3}\|\mathbf{V}\|^2\delta_{\alpha\beta} \right], \quad (55)$$

where we used the fact that $(1/|\Omega|)\sum_{\hat{\omega}}\hat{\omega}\hat{\mathbf{v}}|\hat{\omega}\hat{\mathbf{v}}|_{\beta} = \frac{1}{3}\|\mathbf{V}\|^2\delta_{\alpha\beta}$ for the set of random rotations.

Combining Eqs. (55) and (42) we arrive at the following expressions for the damping factor r_{η} and viscosity coefficient:

$$r_{\eta} = \frac{1 - e^{\rho}}{\rho}, \quad (56)$$

$$\eta = \rho k_B T \frac{\rho + 1 - e^{-\rho}}{2(e^{-\rho} - 1 + \rho)}. \quad (57)$$

IV. SIMULATIONS OF HYDRODYNAMIC FLOWS

In this section we present results of simulations implementing an algorithm based on the present model. The simulations validate the assumptions used in the derivation of hydrodynamic equations and show that the model correctly reproduces fluid flow behavior. Simulations have also been performed to determine the equilibrium velocity distribution and the rate of relaxation to the equilibrium (see Fig. 1).

The nature of the viscous dissipation was determined by simulating flow in the rectangular domain of width $L=30$, density $\rho=10$ and temperature $k_B T=1.0$. In the y -direction we impose bounce-back boundary conditions and the flow is driven by assigning Maxwell-distributed velocities with profile $u_x(y) = 1.2(L-y)y/L^2$ to particles in the region $x < 5$. The results are presented in Fig. 2 and show that the profile is quadratic to a good approximation. The small deviations are due to energy dissipation along the channel and the difference between local equilibrium distribution and the stationary distribution in the Poiseuille flow.

The model also reproduces hydrodynamic flows on larger scales. In Fig. 3 we present the results of simulations of flow past a disk. The system size is 360×120 and the disk diameter $2a=32$. The flow is induced by assigning

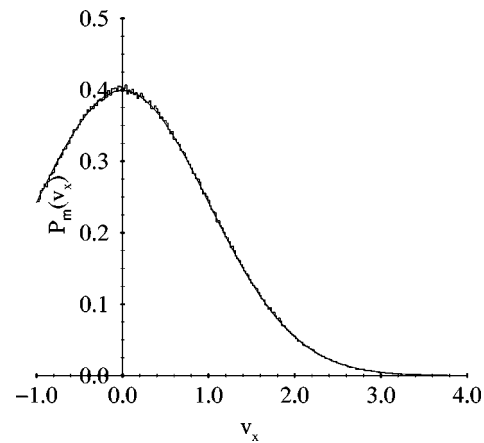


FIG. 1. Velocity distribution: Maxwell velocity distribution (solid line); histogram of v_x distribution computed in simulation (x-step line).

Maxwell-distributed velocities with temperature $T=1$ and velocity $u_x=0.5$ to particles in the region $x < 8$. Periodic boundary conditions are imposed in y direction. For particle density $\rho=10.0$, the kinematic viscosity coefficient (47) is $\nu=0.055$ and the corresponding Reynolds number $Re = 2au_x/\nu = 288$.

The flow was sampled on a set of predefined points by averaging velocities of nearby particles with weights $1/(r^4 + 100)$, where r is the distance between a test point and a particle. After a transient time a flow is established at short distances from the object; however, a flow tail grows indefinitely until it occupies the entire system length. In experiments on fluid flows for these values of the Reynolds number the existence of von Karman streets is documented¹⁴ (see Fig. 4.12.6 of Batchelor). The density of the fluid is nearly uniform and velocity randomization at the boundary eliminates the feedback due to the periodic boundary conditions in the system.

As another illustration of the method in Fig. 4 we present the results of simulations of the stages in the development of the boundary layer at the rear of a disk suddenly set in motion. The system size is 400×400 and the disk diameter $2a=100$. The flow velocity at $x=0$, the density of the system and the Reynolds number are $u_x=0.4$, $\rho=20.0$,

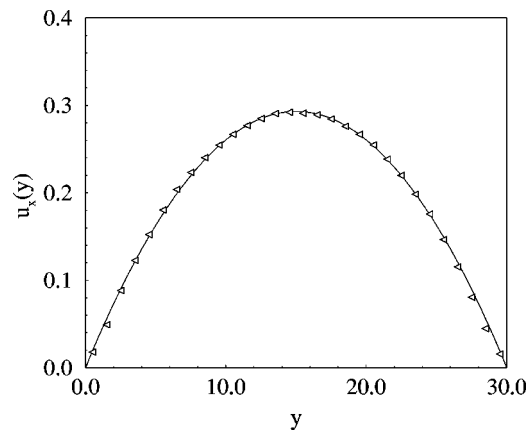


FIG. 2. Poiseuille flow profile: The solid line is a quadratic fit to the computed velocity distribution (triangles).

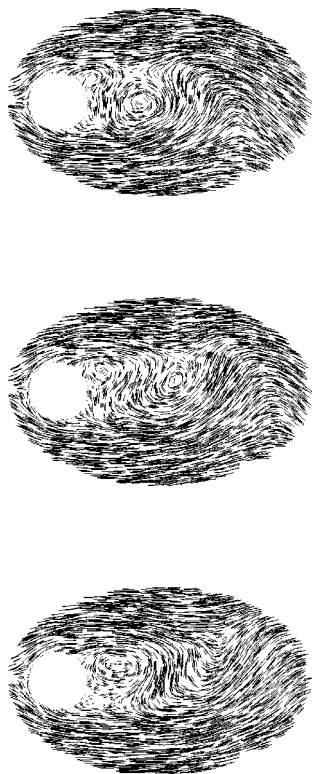


FIG. 3. Vortex shedding in a stationary flow past circular cylinder. The dark line segments represent tangents to the velocity field at their median point. The length of a segment is proportional to the magnitude of the velocity.

and $Re = 1520$, respectively. The system setup is the same as in the simulations of von Karman streets. The initially symmetric flow separates from the disk and a backflow at the far end of the disk develops. At the contact line between the normal flow and the oppositely-directed backflow, a system of vortices appears which later expands into the full-scale boundary layer (cf. Fig. 5.9.3. in Ref. 14).

V. CONCLUSION

The multiparticle-collision stochastic model combines advantageous features of both Direct Simulation Monte Carlo and lattice gas methods for simulations of fluid flows. It differs from DSMC and its variants in the nature of the collision rule. In DSMC collisions in a cell are carried out sequentially on randomly chosen pairs of particles in the cell. This rule leads to exponentially distributed collision times, and the possibility of multiple collisions involving the same particle affects the efficiency of the algorithm. In general, by allowing only pairwise collisions DSMC imposes a high lower bound on the accessible values of the kinematic viscosity coefficient, which may be important if higher Reynolds number flows are desired. Since it is a particle-based scheme the multiparticle-collision model does not suffer from numerical instabilities. The velocity distribution is Maxwellian and the hydrodynamic equations are isotropic.

Because of these features it can serve as mesoscopic model for solvent dynamics which can be coupled to a full molecular dynamics treatment of solute degrees of freedom. The examples of simulations of fluid flow around large ob-

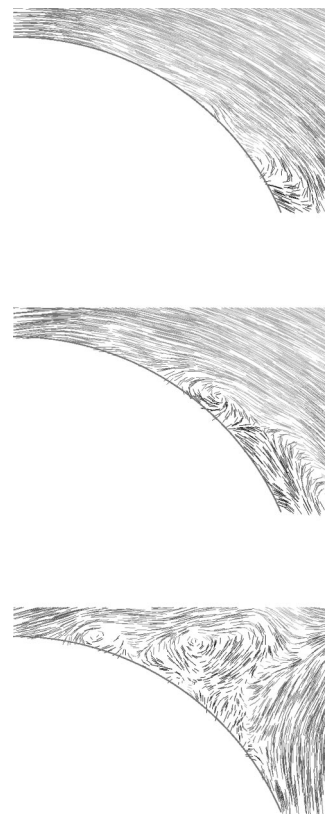


FIG. 4. Development of the boundary layer in flow past disk set in motion.

jects presented in Sec. IV are relevant for studies of the interactions among large colloidal particles in solution. The method has also been used to study the coupling among small ‘effective’ monomer units in a polymer through solvent dynamics.¹⁵ This is an example of the coupling of the full molecular dynamics of a polymer chain to the mesoscale dynamics of the solvent. Consequently one may study the validity of existing polymer models and the influence of fluid flow on polymer conformational dynamics. The collision model is easily extended to treat more complex situations such as the inclusion of interactions that give rise to phase segregation or reactive hydrodynamic flows. To simulate this effect the motion of a small number of complex solute molecules is coupled to the solvent through interaction potentials that affect motion of the ideal particles during the streaming step while preserving the integrals of motion and the phase space volume. The model also may be used to probe the dynamics on mesoscopic length scales where fluctuations may play a role in determining the character of the phenomena.

The emphasis in this paper was both on the formulation of the multiparticle collision model and the development of its theoretical underpinnings, namely, the existence of an H theorem and the derivation of hydrodynamic equations. The simulations have served to verify the theoretical predictions and demonstrate that the model can be used to simulate fluid flows for applications to the dynamics of complex fluids.

ACKNOWLEDGMENT

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APPENDIX: PROOF OF H-THEOREM

In this Appendix we show that $H(t)$ defined in Eq. (21) decreases on each evolution step. The proof of the H-theorem relies on the following convexity inequality:

$$\sum_s A(s)B(s)\ln B(s) \geq \left(\sum_s A(s)B(s) \right) \ln \left(\sum_s A(s)B(s) \right), \quad (\text{A1})$$

where A is normalized by $\sum_s A(s) = 1$.

Introducing the quantity $R^{(n)}$ defined as

$$R^{(n)}(\mathbf{V}^{(n)}, \check{\mathbf{V}}^{(n)}) = \frac{1}{\|\Omega\|} \sum_{\omega \in \Omega} \prod_{i=1}^n \delta(\mathbf{v}_i - \mathbf{V} + \hat{\omega}[V - \check{\mathbf{v}}_i]), \quad (\text{A2})$$

whose integral over $\check{\mathbf{V}}^{(n)}$ is unity, we may rewrite Eq. (20) as

$$H(t) = \sum_{\xi, n \in \mathbb{N}} \frac{e^{-\rho\xi}}{n!} \int_{\mathcal{V}^n} d\mathbf{V}^{(n)} d\mathbf{X}^{(n)} \prod_{i=1}^n f(\mathbf{v}_i, \mathbf{x}_i, t) \times \ln \prod_{i=1}^n f(\mathbf{v}_i, \mathbf{x}_i, t) \int d\check{\mathbf{V}}^{(n)} R^{(n)}(\mathbf{V}^{(n)}, \check{\mathbf{V}}^{(n)}). \quad (\text{A3})$$

In each term in the above sum we exchange the order of the $\check{\mathbf{V}}^{(n)}$ and $\mathbf{V}^{(n)}$ integrations. Use of the convexity inequality (A1) leads to the following relation:

$$\int d\mathbf{V}^{(n)} R^{(n)}(\mathbf{V}^{(n)}, \check{\mathbf{V}}^{(n)}) \prod_{i=1}^n f(\mathbf{v}_i, \mathbf{x}_i, t) \ln \prod_{i=1}^n f(\mathbf{v}_i, \mathbf{x}_i, t) \geq \tilde{f}^{(n)}(\check{\mathbf{V}}^{(n)}, \mathbf{X}^{(n)}, t) \ln \tilde{f}^{(n)}(\check{\mathbf{V}}^{(n)}, \mathbf{X}^{(n)}, t), \quad (\text{A4})$$

where

$$\tilde{f}^{(n)}(\check{\mathbf{V}}^{(n)}, \mathbf{X}^{(n)}, t) = \int d\mathbf{V}^{(n)} R^{(n)}(\mathbf{V}^{(n)}, \check{\mathbf{V}}^{(n)}) \prod_{i=1}^n f(\mathbf{v}_i, \mathbf{x}_i, t). \quad (\text{A5})$$

Hence, we may write

$$H(t) \geq \sum_{\xi, n \in \mathbb{N}} \frac{e^{-\rho\xi}}{n!} \int_{\mathcal{V}^n} d\check{\mathbf{V}}^{(n)} d\mathbf{X}^{(n)} \tilde{f}^{(n)}(\check{\mathbf{V}}^{(n)}, \mathbf{X}^{(n)}, t) \times \ln \tilde{f}^{(n)}(\check{\mathbf{V}}^{(n)}, \mathbf{X}^{(n)}, t). \quad (\text{A6})$$

If we define the quantities Z and $\hat{f}^{(n)}$ as

$$Z = \int_{\mathcal{V}^n} d\check{\mathbf{V}}^{(n)} d\mathbf{X}^{(n)} \tilde{f}^{(n)}(\check{\mathbf{V}}^{(n)}, \mathbf{X}^{(n)}, t) = \rho_\xi^n, \quad (\text{A7})$$

$$\hat{f}_i^{(n)}(\check{\mathbf{v}}_i, \mathbf{x}_i, t) = \frac{1}{Z} \int_{\mathcal{V}_{[n-1]}} d\check{\mathbf{v}}_1 d\mathbf{x}_1 \cdots d\check{\mathbf{v}}_{i-1} d\mathbf{x}_{i-1} \cdots d\check{\mathbf{v}}_n d\mathbf{x}_n \tilde{f}^{(n)}(\check{\mathbf{V}}^{(n)}, \mathbf{X}^{(n)}, t), \quad (\text{A8})$$

where the hat over the integration variables in definition (A8) indicates that these variables should be omitted in the integration, and let

$$A = \prod_{i=1}^n \hat{f}_i^{(n)},$$

$$B = \frac{\tilde{f}^{(n)}(\check{\mathbf{V}}^{(n)}, \mathbf{X}^{(n)}, t)}{Z \prod_{i=1}^n \hat{f}_i^{(n)}},$$

in the inequality (A1) we obtain

$$\frac{1}{Z} \int_{\mathcal{V}^n} d\check{\mathbf{V}}^{(n)} d\mathbf{X}^{(n)} \tilde{f}^{(n)}(\check{\mathbf{V}}^{(n)}, \mathbf{X}^{(n)}, t) \ln \frac{\tilde{f}^{(n)}(\check{\mathbf{V}}^{(n)}, \mathbf{X}^{(n)}, t)}{Z \prod_{i=1}^n \hat{f}_i^{(n)}} \geq \int_{\mathcal{V}^n} d\check{\mathbf{V}}^{(n)} d\mathbf{X}^{(n)} \frac{\tilde{f}^{(n)}(\check{\mathbf{V}}^{(n)}, \mathbf{X}^{(n)}, t)}{Z} \ln \int_{\mathcal{V}^n} d\check{\mathbf{V}}^{(n)} d\mathbf{X}^{(n)} \times \frac{\tilde{f}^{(n)}(\check{\mathbf{V}}^{(n)}, \mathbf{X}^{(n)}, t)}{Z} = 0. \quad (\text{A9})$$

The last equality follows from the fact that the argument of the logarithm is unity in view of the definition of Z . From this inequality we deduce that

$$\int_{\mathcal{V}^n} d\check{\mathbf{V}}^{(n)} d\mathbf{X}^{(n)} \tilde{f}^{(n)}(\check{\mathbf{V}}^{(n)}, \mathbf{X}^{(n)}, t) \ln \tilde{f}^{(n)}(\check{\mathbf{V}}^{(n)}, \mathbf{X}^{(n)}, t) \times \int_{\mathcal{V}^n} d\check{\mathbf{V}}^{(n)} d\mathbf{X}^{(n)} \tilde{f}^{(n)}(\check{\mathbf{V}}^{(n)}, \mathbf{X}^{(n)}, t) \ln Z \prod_{i=1}^n \hat{f}_i^{(n)}. \quad (\text{A10})$$

Finally, using the identity,

$$\sum_{i=1}^n \int_{\mathcal{V}^n} d\check{\mathbf{v}}_i d\mathbf{x}_i Z \hat{f}_i^{(n)}(\check{\mathbf{v}}_i, \mathbf{x}_i, t) \ln Z^{1/n} \hat{f}_i^{(n)}(\check{\mathbf{v}}_i, \mathbf{x}_i, t) = \int_{\mathcal{V}^n} d\check{\mathbf{V}}^{(n)} d\mathbf{X}^{(n)} \tilde{f}^{(n)}(\check{\mathbf{V}}^{(n)}, \mathbf{X}^{(n)}, t) \ln Z \prod_{i=1}^n \hat{f}_i^{(n)}(\check{\mathbf{v}}_i, \mathbf{x}_i, t),$$

we establish the following relation from Eq. (A6):

$$H(t) \geq \sum_{i, \xi, n \in \mathbb{N}} \frac{e^{-\rho\xi} \rho_\xi^{n-1}}{n!} \int_{\mathcal{V}} d\check{\mathbf{v}} d\mathbf{x} Z^{1/n} \hat{f}_i^{(n)}(\check{\mathbf{v}}, \mathbf{x}, t) \times (\check{\mathbf{v}}, \mathbf{x}, t) \ln Z^{1/n} \hat{f}_i^{(n)}(\check{\mathbf{v}}, \mathbf{x}, t) \geq \int d\check{\mathbf{v}} d\mathbf{x} \mathcal{C}(f) \ln \mathcal{C}(f) = \int d\check{\mathbf{v}} d\mathbf{x} f(\check{\mathbf{v}}, \mathbf{x}, t+1) \ln f(\check{\mathbf{v}}, \mathbf{x}, t+1). \quad (\text{A11})$$

In the above expression the inequality (A) arises from applying inequality (A1) with A given by the Poisson distribution $A(n) = (e^{-\rho\xi} \rho_\xi^{n-1} / (n-1)!)$ and equality (B) follows from the invariance of the integral with respect to translations by the streaming transformation. Consequently, the value of the H functional at time $t+1$ does not exceed its value at time t .

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