Discrete Boltzmann Equation for Microfluidics

Baoming Li and Daniel Y. Kwok*
Nanoscale Technology and Engineering Laboratory, Department of Mechanical Engineering, University of Alberta, Edmonton, Alberta T6G 2G8, Canada

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We propose a discrete Boltzmann model for microfluidics based on the Boltzmann equation with external forces using a single relaxation time collision model. Considering the electrostatic interactions in microfluidics systems, we introduce an equilibrium distribution function that differs from the Maxwell-Boltzmann distribution by an exponential factor to represent the action of an external force field. A statistical mechanical approach is applied to derive the equivalent external acceleration force exerting on the lattice particles based on a mean-field approximation, resulting from the electrostatic potential energy and intermolecular potential energy between fluid-fluid and fluid-substrate interactions.

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Computer simulations of microfluidic dynamic problems involving microscale interfacial interactions are of both fundamental and practical importance [1–3]. These interfacial electrokinetic and intermolecular interactions occurring in microfluidic systems affect strongly the physical and chemical properties of the fluid and substantially influence the heat, mass, and momentum transport. Traditional computational fluid dynamics methods for macroscopic hydrodynamic equations have many difficulties in this area due to the presence of an electrical double layer (EDL) between the fluid and channel wall. Since such complexity is essentially due to microscopic interparticle interactions, lattice Boltzmann simulation provides an excellent alternative to model such a complex fluid dynamics problem [4–6].

In this Letter, we propose a discrete Boltzmann equation for microfluidics that is based on the continuous Boltzmann equation using a single-relaxation-time approximation (Bhatnagar-Gross-Kooky collision model). A computational scheme using the derived discrete Boltzmann equation for microfluidics will be briefly discussed. Considering electrostatic interactions in microfluidic systems, we use an equilibrium distribution function that differs from the Maxwell-Boltzmann distribution by a factor (Boltzmann factor) to represent the action of an external force field. A statistical mechanical approach is applied to derive the equivalent external acceleration force exerting on the lattice particles by means of the electrostatic potential energy, intermolecular potential energy between a pair of fluid molecules, and substrate potential energy due to the interactions between the fluid and substrate. The effect of the external force on flow properties is formally absorbed into the equilibrium distribution. The continuous Boltzmann equation is then discretized in the velocity space in a way which guarantees that the Navier-Stokes equation can be obtained at a macroscopic level.

We start with the following continuous Boltzmann equation using a single-relaxation-time approximation as a collision model:

$$\frac{\partial f}{\partial t} + \xi\nabla f + F\nabla_{\xi} f = -\frac{f - f^{\mathrm{eq}}}{\lambda}, \tag{1}$$

where $f \equiv f(x, \xi, t)$ is the single-particle distribution function in the phase space (x, ξ), and ξ is the microscopic velocity; F is an external force vector which can depend on both space and time, λ is a relaxation time due to collision, and f^{eq} is an equilibrium distribution function. At steady state, a fluid in microfluidic systems with a conservative force field is characterized by a distribution function that differs from the Maxwell-Boltzmann distribution by an exponential factor (known as the Boltzmann factor):

$$f^{\mathrm{eq}} = \frac{\rho}{(2\pi c_s^2)^{D/2}} \exp\left[-\frac{U(x)}{k_B T}\right] \exp\left[-\frac{(\xi - u)^2}{2c_s^2}\right], \tag{2}$$

where ρ is the fluid density, k_B is the Boltzmann constant, and $U(x)$ is the potential energy of conservative force field; c_s and D are the sound speed in a fluid and dimension of space, respectively. The macroscopic density ρ, velocity u, and energy ϵ are calculated as the moments of the distribution function f by

$$\rho = \int f d\xi, \tag{3}$$

$$\rho u = \int \xi f d\xi, \tag{4}$$

$$\rho\epsilon = \frac{1}{2}\int (\xi - u)^2 f d\xi. \tag{5}$$

Martys *et al.* [7] pointed out that $F\nabla_{\xi} f$ is identical to $F\nabla_{\xi} f^{\mathrm{eq}}$ up to second order because the first two Hermite coefficients of the distribution function are always the

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same as those in the local Maxwellian distribution. Thus, we assume

$$\nabla_\xi f \approx \nabla_\xi f^{\mathrm{eq}} = -\frac{\xi - u}{c_s^2} f^{\mathrm{eq}} \tag{6}$$

and, consequently, obtain

$$\frac{\partial f}{\partial t} + \xi \nabla f + \frac{1}{\lambda} f = \left(\frac{1}{\lambda} + \frac{F(\xi - u)}{c_s^2} \right) f^{\mathrm{eq}}. \tag{7}$$

We note that the term $[F(\xi - u)/c_s^2]^{-1}$ in the above equation is of the unit of time; hence, we introduce

$$\frac{1}{\lambda'} = \frac{1}{\lambda} + \frac{F(\xi - u)}{c_s^2} \tag{8}$$

as the reciprocal of equivalent relaxation time due to the action of an external force. Accounting for local information at each collision, we obtain the evolution equation of the distribution function f with discrete time as

$$\begin{aligned} &f(x + \xi\delta_t, \xi, t + \delta_t) - f(x, \xi, t) \\ &\quad = -\frac{1}{\tau}\left[f(x, \xi, t) - \frac{\lambda}{\lambda'} f^{\mathrm{eq}}(x, \xi, t) \right], \end{aligned} \tag{9}$$

where $\tau \equiv \lambda/\delta_t$ is a dimensionless relaxation time. In most microfluidic systems, the fluid is in contact with a plane (surface) which is charged and chemically heterogeneous. The charged surface causes a redistribution of ions in the fluid near the surface and results in an EDL. Thus, transport of microfluid by means of an external pressure is retarded by the presence of the double layer (EDL). On the contrary, the EDL induces fluid flow when an external electric field (electro-osmosis) is applied. This is known as the electrokinetic phenomena.

In the lattice Boltzmann Eq. (9), the external force term experienced by each particle can be expressed as

$$F = F_{\mathrm{ext}} + q_\alpha (E_{\mathrm{int}} + \xi \times B_{\mathrm{int}}) + F_V, \tag{10}$$

where F_{ext} represents the external body forces, E_{int} and B_{int} are, respectively, internally smoothed electric and magnetic fields due to the motion of all charged particles inside the fluid (e.g., the space charge in the microfluidics), and F_V is a single equivalent force due to intermolecular potential energy. To obtain an equivalent force exerting on the lattice particles in the mean-field approximation, we employ the canonical ensemble, in which a thermodynamic equilibrium state of the lattice system is uniquely specified by the temperature T, volume $V_f = As_\alpha$, and number of fluid molecules N_f; A is the surface area of a square lattice space defined as δ_x^2, and, hence, $s_\alpha = \delta_x (\alpha = x, y, z)$. Here we consider a cubic lattice space with $A = \delta_x^2$ corresponding to the area of a direct face of the lattice space. Since the lattice system is thermally open to its environment, an infinitesimal, reversible transformation of the lattice is governed by Helmholtz's fundamental relation in differential form as

$$\begin{aligned} dF_H &= -SdT + \mu dN_f + T_{xx}Ads_x + T_{yy}Ads_y + T_{zz}Ads_z \\ &= -SdT + \mu dN_f + dW, \end{aligned} \tag{11}$$

where $F_H = U - TS$ is the Legendre transformation of the internal energy U, S is the entropy, N_f is the number of molecules accommodated by the lattice, and $T_{\alpha\alpha}$ ($\alpha = x, y, z$) are diagonal elements of the stress tensor T associated with the exchange of compressional work W as

$$dW = \sum_\alpha T_{\alpha\alpha} Ads_\alpha. \tag{12}$$

The well-known statistical thermodynamic relation is applied to establish the linkage to the molecular scale. Knowing the canonical partition function χ and treating the fluid particles as independent and indistinguishable, we obtain the Helmholtz free energy of the fluid in the chosen lattice.

$$F_H(T, V_f, N_f) = -\beta^{-1} \ln \chi, \tag{13}$$

where $\beta = 1/k_B T$; $V_f = \delta_x^3$ is the volume of the lattice. The canonical partition function for a classical system in which the molecules possess only a translational degree of freedom is expressed as

$$\chi(T, V_f, N_f) = \frac{1}{N_f! \Lambda^{3N_f}} Z_{N_f}(T, V_f, N_f), \tag{14}$$

where Λ represents the thermal de Broglie wavelength and Z_{N_f} is the configurational integral defined as

$$\begin{aligned} Z_{N_f}(T, V_f, N_f) &= \int_{V_f^{N_f}} dr^{N_f} \exp(-\beta U) \\ &= \prod_{i=1}^{N_f} \int \exp(-\beta U) dr. \end{aligned} \tag{15}$$

For the lattice configuration in microfluidic systems, the configurational energy U can be written as

$$U = U_{\mathrm{ES}} + U_{\mathrm{FF}} + U_{\mathrm{FS}}, \tag{16}$$

where U_{ES}, U_{FF}, and U_{FS} represent the interaction potential energy contributed by electrostatics (ES), fluid-fluid (FF), and fluid-substrate (FS) interactions, respectively, in the system. The electrostatic energy contribution U_{ES} can be obtained by summing over all ions in the chosen lattice:

$$U_{\mathrm{ES}} = \sum_i q_i [\psi(r_i) - \psi_{\mathrm{ref}}]. \tag{17}$$

$\psi(r_i)$ is the potential of the electrostatic field situated at r_i. ψ_{ref} is the reference electrostatic potential which is a constant. The fluid-fluid contribution of the potential energy U_{FF} is given by

$$U_{\mathrm{FF}} = \frac{1}{2} \sum_{i=1}^{N_f} \sum_{j=1 \neq i}^{N_f} u_{\mathrm{ff}}(r_{ij}), \tag{18}$$

where

$$u_{\mathrm{ff}}(r_{ij}) = 4\epsilon_{\mathrm{ff}}\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] \tag{19}$$

is the pairwise additive Lennard Jones 12:6 potential; ϵ_{ff} is the well depth of the fluid-fluid interactions, σ is the molecular hard-sphere diameter, and r_{ij} is the distance between a pair of molecules i and j as

$$r_{ij} = |r_{ij}| = \sqrt{(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2}.$$

The fluid-substrate contribution of the potential energy can be expressed as

$$U_{\mathrm{FS}} = \sum_{i=1}^{N_f} \Phi(x_i, y_i, z_i), \tag{20}$$

where Φ is a mean-field potential. We adopt a mean-field representation of the interaction between a fluid molecule with the substrate. This is obtained by averaging the fluid-substrate interaction potential over the positions of substrate atoms in the x-y plane. As illustrated in Ref. [8], substrate atoms are assumed to be of the same diameter (σ) which occupies the sites of the face centered cubic (fcc) lattice having a lattice constant l, with δ_l as the spacing between successive crystallographic planes in the $\pm z$ direction. We also include nanoscale heterogeneity of the substrate by representing $\epsilon = \epsilon_{\mathrm{fs}}$ [i.e., $u_{\mathrm{fs}}(r)$] as the interaction of a fluid molecule with a substrate atom in the strong cell, and $\epsilon = \epsilon_{\mathrm{fw}}$ [i.e., $u_{\mathrm{fw}}(r)$] as the interaction of a fluid molecule with a substrate atom in the weak cell. The resulting mean-field potential can be expressed as

$$\Phi(x, y, z) = n_A \sum_{m=0}^{\infty} \int_{y_a}^{y_b} dy' \int_{x_a}^{x_b} dx' u_{\mathrm{fs}}(|r - r'|), \tag{21}$$

where $n_A = 2/l^2$ is the areal density of the (100) plane for the fcc lattice. In the above integral, x_a and x_b refer to integration limits in the x direction; y_a and y_b refer to those in the y direction. The symbol m is the mth successive crystallographic plane of substrate in the $\pm z$ direction. According to Eq. (11) and consistent with the fundamental equation, we can define the thermodynamic expression

$$AT_{\alpha\alpha} = \left(\frac{\partial F_H}{\partial s_\alpha}\right)_{T, N_f, s_\beta}. \tag{22}$$

The above equation can be rewritten as

$$T_{\alpha\alpha} = -(A\beta\chi)^{-1}\frac{1}{N_f!\Lambda^{3N_f}}\frac{\partial}{\partial s_\alpha} \times \left\{\prod_{i=1}^{N_f}\int \exp[-\beta(U_{\mathrm{ES}} + U_{\mathrm{FF}} + U_{\mathrm{FS}})]dr\right\}. \tag{23}$$

Differentiation of Eq. (23) yields three terms which we group as

$$T_{\alpha\alpha} = T_{\alpha\alpha,\mathrm{ES}} + T_{\alpha\alpha,\mathrm{FF}} + T_{\alpha\alpha,\mathrm{FS}}. \tag{24}$$

We introduce the probability density function $f_{T,V_f,N_f}(r^{N_f}, N_f)$ of the canonical ensemble as

$$f_{T,V_f,N_f}(r^{N_f}, N_f) = \frac{1}{\chi}\frac{1}{N_f!\Lambda^{3N_f}}\exp[-\beta U]. \tag{25}$$

Thus, one can find the electrostatic field contribution by

$$T_{\alpha\alpha,\mathrm{ES}} = \frac{1}{A}\int_{V_f^{N_f}} dr^{N_f} f_{T,V_f,N_f}(r^{N_f}, N_f)\frac{\partial U_{\mathrm{ES}}}{\partial s_\alpha} = \frac{1}{V_f}\left\langle s_\alpha \frac{\partial U_{\mathrm{ES}}}{\partial s_\alpha}\right\rangle, \tag{26}$$

where the term $\langle s_\alpha \partial U_{\mathrm{ES}}/\partial s_\alpha\rangle$ is Clausius's virial for the electrostatic potential energy with the fluid-fluid contribution given by

$$T_{\alpha\alpha,\mathrm{FF}} = \frac{1}{V_f}\left\langle s_\alpha \frac{\partial U_{\mathrm{FF}}}{\partial s_\alpha}\right\rangle. \tag{27}$$

Similarly, $\langle s_\alpha \partial U_{\mathrm{FF}}/\partial s_\alpha\rangle$ is Clausius's virial for the fluid-fluid intermolecular potential energy. The fluid-substrate contribution is defined by

$$T_{\alpha\alpha,\mathrm{FS}} = -\frac{1}{A}\int_{V_f^{N_f}} dr^{N_f} f_{T,V_f,N_f}(r^{N_f}, N_f)\left[\sum_{i=1}^{N_f}\bar{f}_{\alpha,i}\right] = -\frac{1}{V_f}\left\langle\sum_{i=1}^{N_f} s_\alpha \bar{f}_{\alpha,i}\right\rangle, \tag{28}$$

where

$$\bar{f}_{\alpha,i} = -\frac{\partial\Phi(x, y, z)}{\partial s_\alpha}, \qquad \alpha = x, y, z. \tag{29}$$

It has been shown from the above derivation that the thermodynamic properties of the lattice system can be calculated from the molecular expression as ensemble averages. In practice, the Monte Carlo method can be employed to compute the ensemble average without requiring knowledge of the configuration.

Given the proper discretization of phase space, the lattice Boltzmann equation with the appropriate equilibrium distribution function can also be derived. On a square two-dimensional lattice, for example, we obtain the equilibrium distribution function of the 9-bit lattice Boltzmann equation (LBE) model as

$$f_\alpha^{\mathrm{eq}} = \omega_\alpha \rho \exp\left(-\frac{U(x)}{k_B T}\right)\left[1 + \frac{3(e_\alpha u)}{c^2} + \frac{9(e_\alpha u)^2}{2c^4} - \frac{3u^2}{2c^2}\right]. \tag{30}$$

The discrete velocity set on the lattice structure is

$$e_\alpha = \begin{cases} (0, 0), & & \alpha = 0 \\ c(\cos\theta_\alpha, \sin_\alpha), & \theta_\alpha = \frac{\pi}{2}(\alpha - 1) & \alpha = 1, 2, 3, 4, \\ \sqrt{2}c(\cos\theta_\alpha, \sin\theta_\alpha), & \theta_\alpha = \frac{\pi}{2}(\alpha - 5) + \frac{\pi}{4}, & \alpha = 5, 6, 7, 8 \end{cases} \tag{31}$$

and the corresponding weight coefficient set is

$$\omega_\alpha = \begin{cases} \frac{4}{9}, & i = j = 2, \qquad \alpha = 0 \\ \frac{1}{9}, & i = 1, j = 2, \ldots, \qquad \alpha = 1, 2, 3, 4. \\ \frac{1}{36}, & i = j = 1, \ldots, \qquad \alpha = 5, 6, 7, 8 \end{cases} \tag{32}$$

As an illustration, we consider a microfluidic system where the substrate has a linear nanoscale surface heterogeneity such that a constant interaction potential energy U_{FS} gradient exists between the fluid and the substrate (Fig. 1). Thus, the Clausius's virial for the fluid-substrate contribution is proportional to the constant gradient of interaction potential energy. It is anticipated that more fluid molecules will approach the fluid-solid interface where the interaction potential is higher. As there exists a linear gradient of $U_{\mathrm{FS}}(x)$, more molecules will remain on the relatively higher energy sites, leaving the lower energy sites at a lower density. Thus, this results in a stress tensor $T_{xx,\mathrm{FS}}$ in the direction of the streamline, as indicated in Fig. 1. Its magnitude can be large when compared with the thermodynamic pressure that equals the normal stress tensor of a chemically homogeneous substrate. When the fluid is driven by externally applied forces, the induced stress tensor due to such surface heterogeneities may lead to flow slip at the fluid-substrate boundary. This slip velocity and the equivalent slip length can be estimated from the discrete LBE model described here. For a typical Poiseuille flow, if the precollision unknown distribution is set equal to the value of the distribution along the opposite direction, the slip velocity U_s can be obtained as

$$U_s = \frac{2\tau(\tau - 1)}{3\rho\nu} \delta_x^2 F, \tag{33}$$

where ν is the kinematic viscosity of the fluid. Clearly, there will be a nonzero slip velocity as long as $\tau \neq 1$, corresponding to cases where over-relaxation ($\tau > 1$) or short-relaxation ($\tau < 1$) collision of particles occurs inside the lattice system. It can also be found that the slip velocity is directly proportional to the induced stress tensor due to the linear nanoscale heterogeneities on the substrate surface. Therefore, a possible mechanism for fluid slip in microfluidic systems can result from the nanoscale heterogeneities on the substrate surface where the slip velocity is dependent on the gradient of the interaction potential energy between the fluid and substrate.

In summary, a complete discrete Boltzmann equation for microfluidics has been constructed by consideration of externally applied body force, macroscopic internal field, and equivalent external force due to intermolecular potential energy.

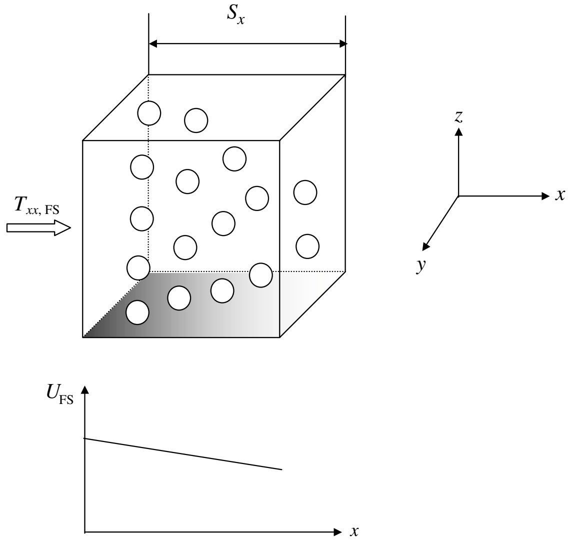

FIG. 1. Schematic of fluid particles in the interfacial lattice where the substrate has a linear nanoscale surface heterogeneity.

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*To whom correspondence should be addressed.

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