

## Simple kinetic model for fluid flows in the nanometer scale

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Fluid flows in the nanometer scale can be studied by molecular dynamics or Monte Carlo methods, but the time and length scales are usually limited to rather short ranges due to the computational expense. Kinetic theory is an alternative tool for studying nanoscale flows, but the existing models are rather complicated and difficult to implement. In this paper, we propose a simple Enskog-like kinetic model for nanoscale flows. The results predicted by this model compare well with molecular dynamics or Monte Carlo simulation results in the literature.

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Understanding the behavior of fluid flows through nanoscale channels is not only of fundamental significance but also essential for the design of various nanodevices. In such small-scale systems, the continuum assumption may break down, and hence the classical continuum hydrodynamic theories will inevitably fail to work [1]. Moreover, on such a small scale, the solid-fluid interaction will become so significant that the fluid properties may become strongly inhomogeneous [2], and hence the conventional kinetic theory for homogeneous fluids is also expected to fail. Under such a circumstance, atomic methods, such as the molecular dynamics (MD) and Monte Carlo (MC) techniques, have become major tools for studying nanoscale fluid flows. However, these atomic methods are usually computationally intensive and limited to phenomena over short time and length scales. Therefore, developing more efficient and practical theory for fluid flows in the nanometer scale is still needed.

Although the conventional kinetic theory is inadequate in studying fluid flows in the nanometer scale, it may serve as a starting point to develop more sophisticated theories. Indeed, a few efforts have been made to extend kinetic theory to nanoscale flows over the past two decades [3–5]. Unlike other statistic-mechanical approaches, such as the sum-rule theory, the density-functional theory (DFT), and the integral equation theory [6], these modified kinetic approaches can be used not only to study the equilibrium properties of nanoscale fluids, but also the transport behavior of nanoscale flows. In fact, some simple planar flows have been studied via the kinetic approach [5,7]. These applications demonstrate the potential of the kinetic approach in the study of nanoscale fluid flows. However, the mentioned models are rather complicated and their applications to general nanoscale flows are difficult and computationally expensive. In this paper, we propose a simple and practical kinetic model for nanoscale fluid flows, and derive the mass and momentum conservation equations.

We consider a fluid composed of classical structureless sphere molecules that interact with a pairwise intermolecular potential  $V(r)$ . Usually  $V(r)$  can be separated into a short-range strong repulsive part  $V_{rep}$  and a long-range weak at-

tractive part  $V_{att}$  [8]. In particular, if  $V_{rep}$  is approximated by a hard-sphere potential the dynamic equation for the one-particle distribution function  $f(\mathbf{r}, \boldsymbol{\xi}, t)$  can be written as [3,9]

$$\begin{aligned} \partial_t f + \boldsymbol{\xi} \cdot \nabla_{\mathbf{r}} f - m^{-1} \nabla_{\mathbf{r}} V_{ext} \cdot \nabla_{\boldsymbol{\xi}} f \\ = m^{-1} \nabla_{\boldsymbol{\xi}} f \cdot \int n(\mathbf{r}_1) \chi(\mathbf{r}, \mathbf{r}_1) \nabla_{\mathbf{r}} V_{att} d\mathbf{r}_1 + J_E, \end{aligned} \quad (1)$$

where  $V_{ext}$  is the external potential,  $m$  is the molecular mass,  $\chi$  is the pair-correlation function (PCF), and  $J_E$  is the Enskog collision operator for hard-sphere fluids [10],

$$J_E(f) \equiv \int [f^{(2)}(\mathbf{r}, \mathbf{r} + \sigma \mathbf{k}, \boldsymbol{\xi}', \boldsymbol{\xi}'_1) - f^{(2)}(\mathbf{r}, \mathbf{r} - \sigma \mathbf{k}, \boldsymbol{\xi}, \boldsymbol{\xi}_1)] d\boldsymbol{\mu}_1. \quad (2)$$

Here  $d\boldsymbol{\mu}_1 = \sigma^2 \Theta(\mathbf{g} \cdot \mathbf{k})(\mathbf{g} \cdot \mathbf{k}) d\mathbf{k} d\boldsymbol{\xi}_1$  is the collision space,  $\sigma$  is the effective diameter of the molecules,  $\mathbf{g} = \boldsymbol{\xi}_1 - \boldsymbol{\xi}$ ,  $\mathbf{k} = (\mathbf{r} - \mathbf{r}_1)/|\mathbf{r} - \mathbf{r}_1|$ ,  $\boldsymbol{\xi}' = \boldsymbol{\xi} + (\mathbf{g} \cdot \mathbf{k})\mathbf{k}$  and  $\boldsymbol{\xi}'_1 = \boldsymbol{\xi}_1 - (\mathbf{g} \cdot \mathbf{k})\mathbf{k}$ , and  $\Theta$  is the Heaviside step function. In the Enskog theory, the two-particle distribution function is approximated by the single-particle distribution function as  $f^{(2)}(\mathbf{r}, \mathbf{r}_1, \boldsymbol{\xi}, \boldsymbol{\xi}_1) = \chi^{hs}(n(\mathbf{r} + \mathbf{r}_1)/2)f(\mathbf{r}, \boldsymbol{\xi})f(\mathbf{r}_1, \boldsymbol{\xi}_1)$ , where  $\chi^{hs}$  is the PCF for homogeneous hard-sphere fluids.

Equation (1) has been introduced intuitively by Davis *et al.* as a base for their theory for nanoscale flows [3]. Nevertheless, the complicated collision operator makes the theory quite difficult in practical applications. Therefore, before preceding to present our kinetic model for nanoscale flows, we first make some bold simplifications to make Eq. (1) more practical while retaining its essential features. To this end, we decompose the collision operator  $J_E$  as  $J_E(f) = J_B(f) + J_{ex}^0(f)$  using the Taylor expansion [10] or projection [11] method, where  $J_B$  is the Boltzmann collision part and  $J_{ex}^0$  is the excess part.  $J_B$  is then approximated by a Bhatnagar-Gross-Krook (BGK)-like model [11],  $J_B(f) = -\lambda^{-1}[f - f^{(eq)}]$ , where  $\lambda$  is a velocity-independent relaxation time, and  $f^{(eq)} = n\phi_l$  is the local equilibrium distribution function, with

$$\phi_l = \left( \frac{m}{2\pi k_B T} \right)^{3/2} \exp \left[ -\frac{m}{2k_B T} (\boldsymbol{\xi} - \mathbf{u})^2 \right]. \quad (3)$$

For an *isothermal* homogeneous fluid,  $J_{ex}^0$  can be approxi-

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mated as [10]  $J_{ex}^0 = -nV_0\chi^{hs}(n)f^{(eq)}(\xi - \mathbf{u}) \cdot \nabla \ln[n^2\chi^{hs}(n)T] + \mathcal{R}$ , where  $V_0 = 2\pi\sigma^3/3$ . The term  $\mathcal{R}$  has no contributions to the mass and momentum, and therefore we can drop  $\mathcal{R}$  from  $J_{ex}^0$  to obtain  $J_{ex}^0 = -V_0f^{(eq)}(\xi - \mathbf{u}) \cdot [2A\chi^{hs}(n) + Bn]$ , where  $A = \nabla n$  and  $B = \nabla\chi$ . Another simplification is made on the attractive part of the potential. It has been demonstrated that the PCF  $\chi$  is approximately unity in the attractive range [12], and so  $\int n(\mathbf{r}_1)\chi(\mathbf{r}, \mathbf{r}_1; n)\nabla_r V_{att}d\mathbf{r}_1 \approx \nabla_r V_m$ , where  $V_m(\mathbf{r}) = \int n(\mathbf{r}_1)V_{att}(\mathbf{r}, \mathbf{r}_1)d\mathbf{r}_1$ . With these simplifications, we now obtain a simplified kinetic model for isothermal homogeneous fluids,

$$\partial_t f + \xi \cdot \nabla_r f - m^{-1}\nabla_r(V_{ext} + V_m) \cdot \nabla_{\xi} f = -\lambda^{-1}[f - f^{(eq)}] + J_{ex}^0. \quad (4)$$

We use Eq. (4) as the starting point of our kinetic model for nanoscale flows. Two problems should be addressed in order to account for the inhomogeneity in nanoscale fluids. The first problem to be addressed is on the extension of  $J_{ex}^0$  to account for the inhomogeneity. It is clear that any suitable extension of  $J_{ex}^0$ , say  $J_{ex}$ , should reduce to  $J_{ex}^0$  in the homogeneous limit. Our extension is

$$J_{ex} = -V_0f^{(eq)}(\xi - \mathbf{u}) \cdot [2\bar{A}\chi^{hs}(\bar{n}) + \bar{B}\bar{n}], \quad (5)$$

where  $\bar{A}(\mathbf{r}) = D^{-1}\int_{|\mathbf{r}'| < \sigma/2} \mathbf{r}' \bar{n}(\mathbf{r} + \mathbf{r}')d\mathbf{r}'$  and  $\bar{B}(\mathbf{r}) = D^{-1}\int_{|\mathbf{r}'| < \sigma/2} \mathbf{r}' \chi^{hs}(\bar{n}(\mathbf{r} + \mathbf{r}'))d\mathbf{r}'$ , with  $D = \pi\sigma^5/120$ . It can be readily shown that, for homogeneous fluids,  $J_{ex}$  does reduce to  $J_{ex}^0$ . The proposed expression for  $J_{ex}$  is inspired by the free-energy DFT for inhomogeneous fluids. It is known that the Helmholtz free energy for an inhomogeneous fluid [13],  $\mathcal{F}$ , can be expressed as  $\mathcal{F} = \mathcal{F}^{att} + \mathcal{F}^{ext} + \mathcal{F}^d + \mathcal{F}^{ex}$ , where the four terms on the right-hand side correspond to the terms  $V_{att}$ ,  $V_{ext}$ ,  $J_B$ , and  $J_{ex}^0$  in Eq. (4) for homogeneous fluids. According to the DFT,  $\mathcal{F}^{ex}$  for inhomogeneous fluids can be modeled as  $\mathcal{F}^{ex} = \int \bar{n}_a \mathcal{F}_0[\bar{n}_b]d\mathbf{r}$ , where  $\bar{n}_a$  and  $\bar{n}_b$  are some weighted densities, and  $\mathcal{F}_0[n]$  is the excess free energy per molecule of a homogeneous hard-sphere fluid of density  $n$ . Motivated by this idea, we appropriate  $J_{ex}(n)$  as  $J_{ex} = J_{ex}^0(\bar{n}_a, \bar{n}_b) = -V_0\bar{n}_a\phi_f(\xi - \mathbf{u}) \cdot [2\bar{A}(\bar{n}_b)\chi^{hs}(\bar{n}_b) + \bar{B}(\bar{n}_b)]$ . By taking  $\bar{n}_a = n$  and  $\bar{n}_b = \bar{n}$ , we obtain the extended  $J_{ex}$  as given by Eq. (5).

It is worth noting that in  $J_{ex}$  defined by Eq. (5), the PCF is approximated by  $\chi = \chi^{hs}(\bar{n})$ . This approximation is consistent with the model introduced by Fischer and Methfessel [14]. They assumed that the unknown PCF in an inhomogeneous fluid can be estimated from a homogeneous fluid PCF, but it is evaluated at a local average density  $\bar{n}$  instead of the local density  $n$ . It has been shown that the FM model could give fairly accurate predictions [3], given that  $\bar{n}$  and  $\chi^{hs}$  are specified properly. The Tarazona average method [15] coupled with the Carnahan-Starling hard-sphere PCF [16] has been shown to be a good choice to specify  $\bar{n}$  and  $\chi^{hs}$  [13], and we will use this choice in our model.

The second problem to be addressed is how to determine the relaxation time  $\lambda$ . Our strategy is based on the local average density model (LADM) [17], in which the shear viscosity  $\mu$  for a nanoscale fluid is modeled by that of a homogeneous fluid with a weighted density, i.e.,  $\mu = \mu(\bar{n})$ . On the

other hand, it is known that for a homogeneous fluid  $\mu$  is related to  $\lambda$  by  $\mu(n) = \lambda nk_B T$  [11]. Therefore, for an inhomogeneous fluid  $\lambda$  can be modeled as  $\lambda(\mathbf{r}) = \mu(\bar{n})/nk_B T$ , such that  $\mu(\mathbf{r}) = \mu(\bar{n}(\mathbf{r}))$ . To complete the approximation, we need a formula for  $\mu$ . Here we use the Enskog expression for hard-sphere fluids given in [10],  $\mu(n) = \mu_0 n V_0 (y^{-1} + 0.8 + 0.7614y)$ , where  $y = nV_0\chi^{hs}(n)$ .

Once  $J_{ex}$  and  $\lambda$  are determined, we can obtain a simple kinetic model for nanoscale fluid flows as follows:

$$\partial_t f + \xi \cdot \nabla_r f - m^{-1}\nabla_r(V_{ext} + V_m) \cdot \nabla_{\xi} f = -\lambda^{-1}[f - f^{(eq)}] + J_{ex}. \quad (6)$$

A Chapman-Enskog analysis of the above equation leads to the following equations for conservative variables:

$$\partial_t(mn) + \nabla \cdot (m\mathbf{n}\mathbf{u}) = 0, \quad (7a)$$

$$\begin{aligned} \partial_t(m\mathbf{n}\mathbf{u}) + \nabla \cdot (m\mathbf{n}\mathbf{u}\mathbf{u}) + k_B T \nabla n + n \nabla (V_{ext} + V_m) \\ = \nabla \cdot (\mu(\bar{n})\bar{\nabla}\mathbf{u}) + nk_B T [2\bar{A}\chi^{hs}(\bar{n}) + \bar{B}\bar{n}]V_0, \end{aligned} \quad (7b)$$

where  $\bar{\nabla}\mathbf{u} = [\nabla\mathbf{u} + (\nabla\mathbf{u})^T]$ . It is noted that for homogeneous fluid flows,  $\bar{A}$  and  $\bar{B}$  reduce to  $A$  and  $B$ , respectively, and Eqs. (7a) and (7b) reduce to the usual Navier-Stokes equations derived from the Enskog theory for dense homogeneous fluid [10]. This means that these equations are applicable to both nanoscale and macroscale fluid flows.

We now apply the proposed kinetic model to study the equilibrium properties of a fluid confined in a planar nanosized slit pore, where the external potential arises from the solid wall located at  $x=0$  and  $x=H$ . In such a system, the inhomogeneity only appears in  $x$  direction. At equilibrium with  $\mathbf{u} = \mathbf{0}$ , Eq. (7b) reduces to a Yvon-Born-Green (YBG)-like equation,

$$\frac{d}{dx} \left( \ln n + \frac{V_{ext} + V_m}{k_B T} \right) = [2\bar{A}_x \chi^{hs}(\bar{n}) + \bar{B}_x \bar{n}]V_0, \quad (8)$$

which can be solved numerically to obtain the equilibrium density distribution in the slit, provided that the external and the intermolecular potentials are given.

As a first application, we calculate the density distribution of a hard-sphere fluid confined between two hard walls. This

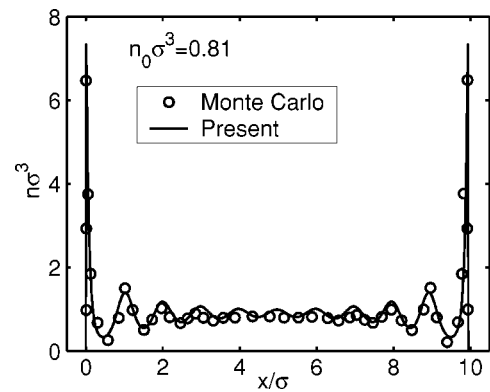


FIG. 1. The density distribution of a hard-sphere fluid confined between two hard walls with a separation of  $10.94\sigma$ .

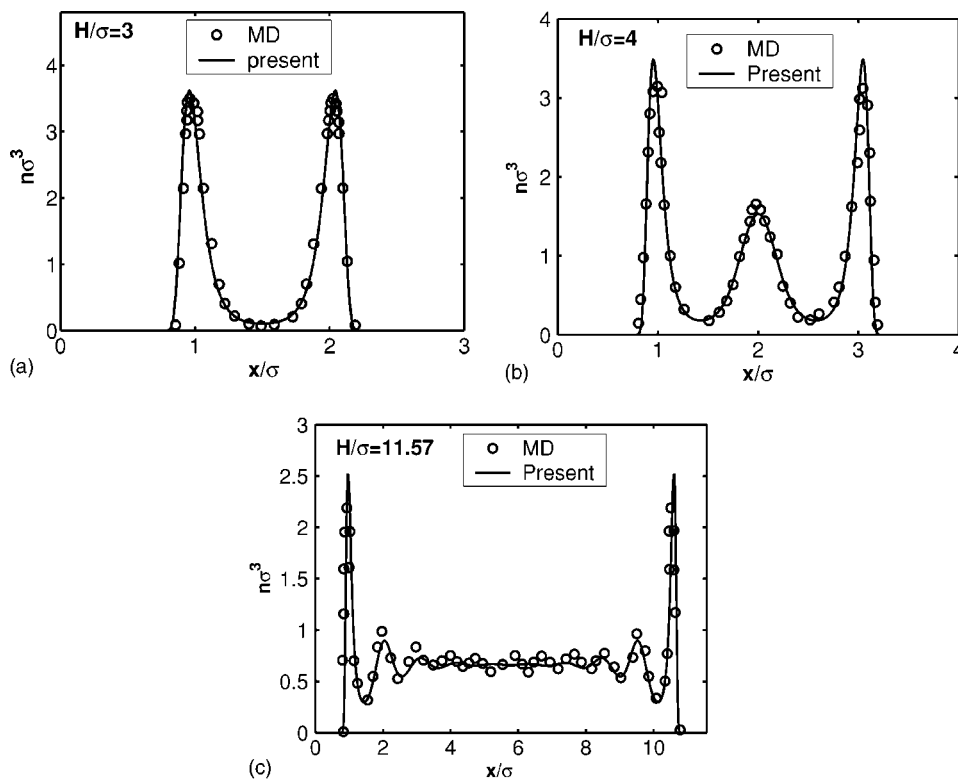


FIG. 2. The density distribution of a Lennard-Jones fluid confined between two 10-4-3 walls ( $\epsilon_w = \epsilon$ ). MD results are taken from [19]. For  $H/\sigma=3$  and 4, the bulk density  $n_b=0.5925\sigma^{-3}$  and temperature  $T=1.2\epsilon/k_B$ ; for  $H/\sigma=11.57$ ,  $n_b=0.67\sigma^{-3}$  and  $T=0.972\epsilon/k_B$ .

problem has been used as a benchmark to test theories for inhomogeneous fluids [13]. The number density is compared with the MC result [18] in Fig. 1, with a pore-averaged density  $n_0 \equiv H^{-1} \int_0^H n(x) dx = 0.81\sigma^{-3}$ . It is seen that the density oscillation in the pore is in quantitative agreement with the MC result, which demonstrates the capability of the present model in predicting the structure induced by the excluded volume effect in a nanoscale fluid.

To further demonstrate the capability of the present model, we apply it to study the equilibrium properties of a Lennard-Jones (LJ) fluid confined between two walls with a 10-4-3 potential [19],  $V_w(r) = 1.6\pi\epsilon_w[0.4z^{10} - z^4 - z^3/2.12(1 + 0.43z)]$ , where  $z = \sigma/r$ . In our computations, the pore-averaged density is taken approximately to be what was used

in the MD simulations. The density profiles at different pore sizes are presented in Fig. 2 and compared with the MD results [19]. Again, good agreement is achieved. In particular, the kinetic model captures the critical change in the fluid structure: a third peak in the central region appears as  $H$  changes from  $3\sigma$  to  $4\sigma$ . As  $H$  reaches 11.57, three pronounced peaks with decaying magnitudes in the vicinity of each wall are observed, and the fluctuation of the density in the core region is rather weak. These results indicate that the proposed kinetic model is also applicable to studying the equilibrium properties of more realistic nanofluids than hard-sphere fluids.

We also applied the proposed model to predict the dynamic behavior of a LJ fluid flowing in a narrow pore. As an example, we present here the results of the planar Couette flow. The two confining wall exert a 10-4 potential (similar

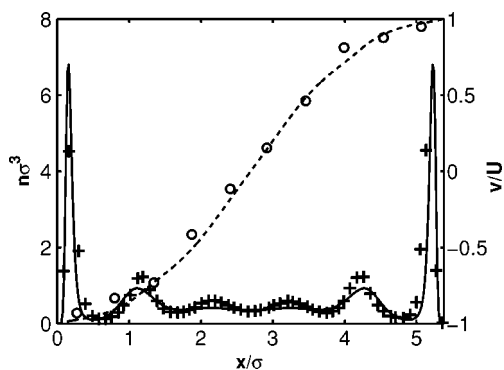


FIG. 3. Density and velocity distributions of the planar Couette flow in a pore of width  $H=5.384\sigma$ . Pore-average density  $n_0 = 0.692\sigma^{-3}$ ; temperature  $T=1.1\epsilon/k_B$ , wall potential energy  $\epsilon_w=4\epsilon$ . Solid and dashed lines: density and velocity predicted by the present kinetic model. Symbols: the MD results in Ref. [17].

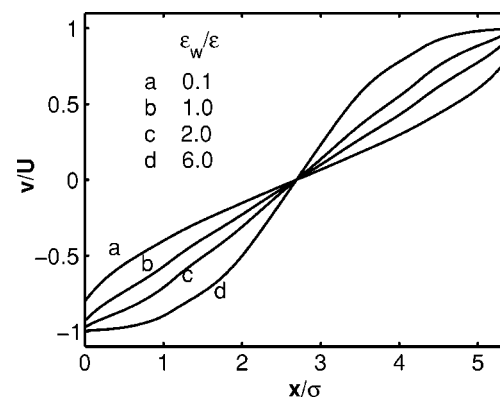


FIG. 4. Velocity distributions against the wall potential for the same system as in Fig. 3.

to the 10-4-3 potential, except without the last term of order 3) [17]. At steady state, the density and velocity distributions can be obtained by solving Eq. (7). In Fig. 3, the density and velocity distributions of one of the simulations are presented. It is observed that the results predicted by the present kinetic model agree well with the MD simulation results [17]. The effective viscosity and shear stress predicted are 0.6623 and 0.1230, respectively, which are in excellent agreement with the MD results,  $0.65 \pm 0.02$  and  $0.121 \pm 0.003$  [17]. It is also evident that, unlike the linear velocity distribution in conventional Couette flows, the velocity profile in the narrow pore deviates greatly from linearity. This deviation is due to the inhomogeneous nature of the nanoscale fluid flow, induced by the wall-fluid interactions. Therefore, it is not surprising that the strength of the wall potential has a significant influence on the velocity distribution. As shown in Fig. 4, under a strong wall-fluid interaction, a layer of fluid atoms is absorbed on the wall and moves with the wall. On the other hand, an obvious velocity slip is observed for a weak wall

potential, and the weaker the potential, the larger the slip. A similar phenomenon was also reported in MD simulations [5,20].

In summary, we have derived an Enskog-like kinetic model for fluid flows in the nanometer scale. The introduction of a BGK-like approximation enables the present model to be much simpler than the other existing models. The good quantitative agreement between the present model predictions and MD as well as MC simulations, which usually consume tremendous computational time, demonstrates that this model is a promising tool for studying nanoscale fluid flows. We also believe that the present model can be extended to allow more complex nanoscale flows to be studied by including other intermolecular interactions, e.g., electrostatic interactions.

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