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Configurational temperature profile in confined fluids. I. Atomic fluid

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Two configurational expressions for the temperature are applied to the calculation of temperature profiles within a confined atomic fluid in a narrow slit pore. The configurational temperatures profiles so obtained are compared to the kinetic temperature, calculated from the equipartition principle, in equilibrium (EMD), and nonequilibrium molecular dynamics (NEMD) simulations of planar Poiseuille flow. We show that one of the configurational expressions exhibits a system-size dependence which prevents its application to the determination of high-resolution temperature profiles. The other expression yields good agreement with the kinetic temperature profile in both equilibrium and nonequilibrium systems. © 2001 American Institute of Physics.

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I. INTRODUCTION

Until very recently, the calculation of temperature in computer simulations was always based on the equipartition principle. This expression of the temperature, that we will term as the kinetic temperature, requires taking averages of the kinetic energy in equilibrium system or of the peculiar kinetic energy in nonequilibrium systems. In nonequilibrium molecular dynamics (NEMD) simulations of a confined atomic fluid undergoing planar Poiseuille flow, the calculation of the peculiar kinetic energy is achieved in a two-stage procedure.^{1–3} The streaming velocity of the fluid is first determined by fitting an assumed profile to the streaming velocity data. The peculiar momenta and hence the peculiar kinetic energies are then calculated by subtraction of the fitted streaming velocity profile. However it is unclear how one might apply this procedure to the study of the flow of long and/or flexible molecules.

Recent work has shown that the thermodynamic temperature can be evaluated solely from configurational information.^{4–8} In these configurational expressions, the temperature is computed from the first and the second spatial derivatives of the intermolecular potential energy. The application of these expressions to the calculation of the temperature in nonequilibrium systems seems promising since it would circumvent the difficult evaluation of the streaming velocity.

The aim of this paper is to apply and to assert the reliability of the configurational expressions of the temperature as applied to the study of confined fluids. Specific difficulties arise in the application of these expressions when one wants to study a confined fluid. Jepps *et al.*⁷ have shown that $O(1/N)$ corrections to the configurational expressions for the temperature exhibit variations with the density and the size of the system studied. Confined fluids exhibit strong variations in the direction of the confinement.^{1–3,9–11} One has to divide the channel into bins to determine a profile. The number of atoms per bin on which the configurational expressions are applied is quite small and thus the issue of the system-size dependence is enhanced in those systems. Two

different expressions for the configurational temperature are tested in this work. In the first place, equilibrium molecular dynamics of a confined atomic fluid is carried out. The kinetic temperature profile is compared with the two configurational approximations to the temperature profiles. We carefully study the system-size dependence of the configurational expressions. We then perform NEMD simulations of Poiseuille flow. In the latter, we first evaluate streaming velocity profiles in order to calculate the peculiar kinetic energy and hence the kinetic temperature. We then compare the temperature profiles obtained using the multistage kinetic and the single stage configurational determination of the temperature profile.

The paper is organized as follows. We first give the mathematical expressions for the configurational temperature used in this work. We then present the simulation details and explain how the temperature profiles are determined. Thereafter, comparisons between the various temperature profiles are drawn in equilibrium and nonequilibrium systems.

II. CONFIGURATIONAL EXPRESSIONS FOR THE TEMPERATURE

A. General expressions

Let us consider an N -atom system. We denote a phase space vector by $\Gamma \equiv (\mathbf{q}_1, \dots, \mathbf{q}_N, \mathbf{p}_1, \dots, \mathbf{p}_N)$, where $\mathbf{q}_N$ is the position coordinate of atom N and $\mathbf{p}_N$ its momentum. We now define a microcanonical (NVE) ensemble for a given Hamiltonian $H(\Gamma) (= K(\mathbf{p}_1, \dots, \mathbf{p}_N) + V(\mathbf{q}_1, \dots, \mathbf{q}_N))$ by the set of phase points, termed as $\mu C(E)$, whose energies lie between E and $E + \delta E$, where $|\delta E| \ll E$, with Boltzmann's equal *a priori* probability assumption. The entropy of this ensemble is related to its phase space volume through

$$S(E) = k_B \ln(V_r(N, V, E)) = k_B \ln \int_{\mu C(E)} d\Gamma. \quad (1)$$

The thermodynamic temperature is obtained through the following differentiation:

$$\frac{1}{T} = \left. \frac{\partial S}{\partial E} \right|_V. \quad (2)$$

Rugh⁴ initially proposed a scheme to evaluate the temperature by calculating this derivative. In this scheme, the phase points Γ of the (NVE) ensemble are displaced to the points Γ' along the phase space gradient of the Hamiltonian,

$$\Gamma'(\Gamma) = \Gamma + \mathbf{n}(\Gamma) \Delta E = \Gamma + \frac{\mathbf{G} \cdot \nabla H(\Gamma)}{\nabla H(\Gamma) \cdot \mathbf{G} \cdot \nabla H(\Gamma)} \Delta E, \quad (3)$$

where ΔE stands for a change in energy of the system. The matrix $\mathbf{G}$ is quite a general matrix.⁴ However it must satisfy the equation,

$$\nabla H(\Gamma) \cdot \mathbf{G} \cdot \nabla H(\Gamma) \neq 0. \quad (4)$$

The entropy of the $(NV(E + \Delta E))$ microcanonical ensemble is

$$S(E + \Delta E) = k_B \ln \int_{\mu C(E + \Delta E)} d\Gamma = k_B \ln \int_{\mu C(E)} J(\Gamma) d\Gamma, \quad (5)$$

where $J(\Gamma)$ is the Jacobian of the transformation $\Gamma \rightarrow \Gamma'$. To first order in ΔE , it is equal to

$$J(\Gamma) = \left| \frac{\partial \Gamma'(\Gamma)}{\partial \Gamma} \right| = 1 + \nabla \cdot \mathbf{n}(\Gamma) \Delta E. \quad (6)$$

Therefore, introducing Eqs. (5) and (6) in Eq. (1), we obtain the following expression for the temperature:

$$\frac{1}{T} = \left. \frac{\partial S}{\partial E} \right|_V = k_B \langle \nabla \cdot \mathbf{n} \rangle. \quad (7)$$

It has been shown that this expression holds for the microcanonical and the canonical ensembles.⁷ If we now choose the matrix $\mathbf{G}$ such as $g_{ij} = \delta_{ij}$ if i and j refer to coordinate variables and 0 otherwise, we obtain

$$\frac{1}{T} = k_B \left\langle \frac{-\sum_i \nabla_i \cdot \mathbf{F}_i}{\sum_i \mathbf{F}_i^2} - \frac{\sum_{ij} \mathbf{F}_i \mathbf{F}_j : \nabla_i \mathbf{F}_j}{(\sum_i \mathbf{F}_i^2)^2} \right\rangle, \quad (8)$$

where the index i (or j) refers to an atom, $\mathbf{F}_i$ represents the force acting on atom i , ∇_i is the gradient vector with respect to the Cartesian coordinates of atom i and $:$ is the dyadic operator (i.e., for vectors $\mathbf{a}, \mathbf{b}$, and matrix $\mathbf{M}$, $\mathbf{a} \cdot \mathbf{b} \cdot \mathbf{M} = \sum_{\alpha, \beta} a_{\alpha} b_{\beta} M_{\beta \alpha}$). This expression is computationally expensive since the second term of the right-hand side of Eq. (8) involves calculations which assume the forces to have already been evaluated, thus requiring a second force loop. However, in the case of a short-ranged potential, this term is of the order of $1/N$ (since $\mathbf{F}_i \mathbf{F}_j : \nabla_i \mathbf{F}_j$ tends to zero for large atomic separations) and vanishes in the thermodynamic limit. We can thus define the following order 1 expression for the temperature:

$$\frac{1}{k_B T_{\text{con1}}} = \frac{\langle -\sum_i \nabla_i \cdot \mathbf{F}_i \rangle}{\langle \sum_i \mathbf{F}_i^2 \rangle}. \quad (9)$$

Jepps *et al.*⁷ have recently provided a more general expression of Rugh's theorem,

FIG. 1. Simulation geometry for planar Poiseuille flow. The z axis is normal to the page.

$$\frac{1}{T} = k_B \frac{\langle \nabla \cdot \mathbf{B}(\Gamma) \rangle}{\langle \nabla H \cdot \mathbf{B}(\Gamma) \rangle}, \quad (10)$$

where $\mathbf{B}(\Gamma)$ is an arbitrary phase space vector field. This expression holds for the microcanonical and the canonical ensemble. We note that if we replace $\mathbf{B}(\Gamma)$ by $\mathbf{n}(\Gamma)$, we obtain Rugh's expression. If we now substitute $\mathbf{G} \cdot (\nabla H)$ for $\mathbf{B}(\Gamma)$, we obtain a second configurational expression for the temperature, termed as T_{conf} (the label "F" indicates that this expression is a fraction of two averages),

$$\frac{1}{k_B T_{\text{conf}}} = \frac{\langle -\sum_i \nabla_i \cdot \mathbf{F}_i \rangle}{\langle \sum_i \mathbf{F}_i^2 \rangle}. \quad (11)$$

B. Application to confined systems

In this section, we explain how one can modify the general expressions derived in the previous section to study systems of specific geometries. In the case of a confined fluid, it is of instance of interest to calculate the temperature along the direction of confinement. We use the fact that there is considerable freedom in the choice of matrix $\mathbf{G}$.

If we divide the confined fluid into bins along y (the geometry of the system is shown in Fig. 1) and if we choose $\mathbf{G}$ such as $g_{ij} = \delta_{ij} \delta_{ib} \delta_{jb}$ if i and j refer to coordinate variables (δ_{ib} is equal to 1 if the atom associated with i is located into bin, b) and 0 otherwise, we obtain for the first order configurational temperature,

$$\langle T_{\text{con1}}(y_b) \rangle = \left\langle \frac{-\sum_{i=1}^{N_{\text{bin}}} \nabla_i \cdot \mathbf{F}_i}{\sum_{i=1}^{N_{\text{bin}}} \mathbf{F}_i^2} \right\rangle, \quad (12)$$

and the configurational temperature, as expressed in Eq. (11), is evaluated as

$$\langle T_{\text{conf}}(y_b) \rangle = \frac{\left\langle -\sum_{i=1}^{N_{\text{bin}}} \nabla_i \cdot \mathbf{F}_i \right\rangle}{\left\langle \sum_{i=1}^{N_{\text{bin}}} \mathbf{F}_i^2 \right\rangle}. \quad (13)$$

We note that this one way to compute a configurational temperature profile. There are of course many other possible ways since the matrix $\mathbf{G}$ is not unique. We also add that,

using the property of matrix $\mathbf{G}$, it is possible to derive configurational expressions for any kind of geometry.

III. METHOD

A. Simulation technique

The fluid and the wall atoms are modeled by the same truncated and shifted Lennard-Jones potential. They interact through the following formula:

$$u(r_{ij}) = -4\varepsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^6 - \left(\frac{\sigma}{r_{ij}} \right)^{12} \right] + u(r_c) \quad r \leq r_c, \quad (14)$$

$$u(r_{ij}) = 0 \quad r > r_c,$$

where r_{ij} is the distance between atom i and atom j , r_c is the truncation distance, $u(r_{ij})$ is the value taken by the potential energy at the truncation point, and σ and ε are the distance and energy parameters for the Lennard-Jones potential. In this work, we have used two kinds of truncated and shifted Lennard-Jones potential. The WCA potential¹² is obtained by truncating the Lennard-Jones potential at the distance for which it takes its minimum value ($r_c = 2^{1/6}\sigma$). Since it is truncated at its minimum, the WCA potential is purely repulsive. For computational reasons, most of the simulations were performed using the WCA potential. However, as pointed out by Travis and Gubbins,³ confined fluids simulated using a potential model with or without an attractive contribution do not exhibit the same features. We have therefore carried out a few simulations with a Lennard-Jones potential truncated and shifted at $r_c = 2.5\sigma$. This potential will be referred as LJ in the remainder of this paper.

The walls are three atomic layers thick. There are 3 layers of $N_w = 72$ atoms (which amounts to a total number of atoms $N = 216$), placed in a fcc lattice structure with a surface density of $N_w\sigma^2/(L_x L_z) = 0.615$, where L_x and L_z are the dimensions of the simulation cell along the x and the z axis, respectively, and the layer separation is 1.085σ . The simulation cell is periodic in the three dimensions. There is only one wall three layers thick per simulation cell. The second wall is just the periodic image of the first wall. The wall atoms are kept in place by a combination of harmonic tethering forces¹³ and a constraint mechanism, based on Gauss' principle of least constraint,¹⁴ which fixes the position of each layer of the wall. The walls are also kept at a constant reduced temperature of 0.722 by application of a Gaussian thermostat.¹⁴

The equations of motion for wall atom i are therefore,

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m}, \quad (15a)$$

$$\dot{\mathbf{p}}_i = -K(\mathbf{r}_i - \mathbf{r}_i^{\text{eq}}) + \mathbf{F}_i^{\text{WCA or LJ}} - \alpha \mathbf{p}_i - \mathbf{j} \lambda_{Lj}, \quad (15b)$$

where K is the spring constant of the harmonic tethering potential (fixed to 150.15 in reduced units), $\mathbf{r}_i^{\text{eq}}$ is the equilibrium site of atom i , $\mathbf{F}_i^{\text{WCA or LJ}}$ is the force acting on i due to both wall-wall and wall-fluid interatomic interactions, α is the thermostat multiplier, and λ_{Lj} is the layer multiplier for layer Lj ($j = 1, 2, 3$).

The thermostat multiplier α and the layer multiplier λ_{Lj} are given by

$$\alpha = \frac{N_w \sum_{j=1}^N \mathbf{F}_j \cdot \mathbf{p}_j - \sum_{k=1}^3 (\mathbf{j} \cdot \sum_{i \in Lk}^{N_w} \mathbf{p}_i) (\mathbf{j} \cdot \sum_{i \in Lk}^{N_w} \mathbf{F}_i)}{N_w \sum_{j=1}^N \mathbf{p}_j \cdot \mathbf{p}_j - \sum_{k=1}^3 (\mathbf{j} \cdot \sum_{i \in Lk}^{N_w} \mathbf{p}_i) (\mathbf{j} \cdot \sum_{i \in Lk}^{N_w} \mathbf{p}_i)}, \quad (16)$$

$$\lambda_{Lj} = \frac{\mathbf{j}}{N_w} \sum_{i=1}^{N_w} [-K(\mathbf{r}_i - \mathbf{r}_i^{\text{eq}}) + \mathbf{F}_i^{\text{WCA or LJ}} - \alpha \mathbf{p}_i]. \quad (17)$$

Most of the simulations were performed with 288 fluid atoms. The pore width L_{PW} is chosen to be equal to 4.0σ . There is no unambiguous definition for the volume accessible to the fluid. In line with previous work,¹⁻³ we choose to define the effective pore width as $L_{\text{PWe}} = L_{\text{PW}} - \sigma$. Simulations are thus performed at a reduced density of the fluid of 0.82. The fluid atoms obey Newton's equation of motion,

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m}, \quad (18a)$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i^{\text{WCA or LJ}} (+ \mathbf{i} F_e), \quad (18b)$$

where $\mathbf{F}_i^{\text{WCA or LJ}}$ is now the force acting on i due to both fluid-fluid and wall-fluid interatomic interactions and $\mathbf{i} F_e$ is the external force used to drive the Poiseuille flow along the x axis. The parentheses indicate that this term is only employed in NEMD simulations. It is implied that $\mathbf{p}_i$ is the laboratory momentum of atom i (i.e., the sum of the peculiar and streaming components). It should also be noted that the thermostat is applied to the wall atoms only (in NEMD simulations, viscous heat generated by the fluid is removed by conduction through the walls).

B. Calculation of density and temperature profiles

We used the method of planes to calculate the density profiles.¹⁵ The simulation cell is divided along the y axis into a number (200 in this work) of equally spaced planes of $L_x \times L_z$ area. The number density can then be evaluated at the planes positions according to the following formula:

$$\bar{n}(y) = \lim_{\tau \rightarrow \infty} \frac{1}{\tau A} \sum_i \sum_{0 < t_{\text{cr}(i)} < \tau} \frac{1}{|\dot{y}_i(t_{\text{cr}(i)})|}, \quad (19)$$

where $\bar{n}(y)$ is the mean atomic density at a plane of coordinate y , $\{t_{\text{cr}(i)}\}$ are the times at which the center-of-mass of molecule i crosses the plane of coordinate y and $\dot{y}_i$ is the y component of the velocity of atom i .

In NEMD simulations, the calculation of the kinetic temperature requires computing the averages of the peculiar kinetic energy. We thus need to determine the streaming velocity profile. We first evaluate the momentum density at the planes positions,

$$\bar{J}_x(y) = \lim_{\tau \rightarrow \infty} \frac{1}{\tau A} \sum_i \sum_{0 < t_{\text{cr}(i)} < \tau} \frac{m \dot{x}_i(t_{\text{cr}(i)})}{|\dot{y}_i(t_{\text{cr}(i)})|}, \quad (20)$$

where $\bar{J}_x(y)$ is the average momentum density at y and $\dot{x}_i$ is the x component of the velocity of atom i .

The average streaming velocity is obtained through its definition,

FIG. 2. Number density profiles for a WCA system (dotted line) and a LJ system (straight line) at equilibrium.

$$\bar{u}_x(y) = \frac{\bar{J}_x(y)}{m\bar{n}(y)}. \quad (21)$$

We then fit the streaming velocity profile to a functional form that retains the Navier–Stokes solution (i.e., a quadratic profile) with the addition of a truncated Fourier cosine series,^{2,3}

$$\bar{u}_x(y) = a_0 + a_1 y^2 + \sum_{n \geq 2} a_n \cos\left(\frac{2\pi(n-1)y}{L_{\text{PWe}}}\right), \quad (22)$$

where the quantities $a_0, \dots, a_n$ are fitting parameters.

In separate simulations, we then calculate the temperature profiles of the fluid. For this purpose, we divide the simulation cell along the y axis into 40 bins and evaluate the temperature in each bin in three different ways.

The kinetic temperature is given by

$$\langle T_{\text{kin}}(y_b) \rangle = \frac{\langle \sum_{i=1}^{N_{\text{bin}}} m [\mathbf{v}_i - \bar{\mathbf{u}}_x(y_i)] [\mathbf{v}_i - \bar{\mathbf{u}}_x(y_i)] \rangle}{\langle 3N_b \rangle}. \quad (23)$$

Because separate simulations runs are used to determine $\bar{u}_x(y)$ and $T_{\text{kin}}(y)$, we do not have to reduce the number of degrees of freedom from $3N_b$ in Eq. (23). The temperature is also computed using the configurational expressions given in Eqs. (12) and (13). We note that only one computer simulation run is needed to determine the configurational temperatures. This is because no prior knowledge of the streaming velocity is required in these cases.

The simulations were started by equilibrating an initially crystalline fluid for one million time steps. In NEMD simulations, it was followed by another one million time steps of equilibration with the external field switched on and then, one million time steps in order to determine the streaming velocity profile. Production runs consisted of 4–10 millions time steps in both equilibrium and NEMD simulations with a reduced time step of 0.001.

IV. EQUILIBRIUM SIMULATIONS

The density profiles obtained from simulations of the WCA and the LJ systems are shown in Fig. 2. Normal ordering in WCA or LJ fluids is a well understood phenomenon.^{11,12,16} The oscillations in the density profile re-

FIG. 3. Temperature profile for a WCA system using the peculiar kinetic energy (filled circles) or the configurational expressions T_{con1} (open squares) or T_{conf} (open diamonds).

sult from structure in the fluid pair correlation function and the sharp cutoff in the fluid density at the wall. For both systems, we observe high density peaks near the walls associated with well-defined fluid layers. One can see from the case of the LJ fluid that a higher density is observed close to the walls when attractive forces are taken into account. Further ordering is then induced along the y axis and yields a density profile exhibiting five peaks for the LJ fluid as compared to three for the WCA fluid. We also note that in both cases, the density profile falls to essentially zero well before the walls' location of $y^* = \pm 2.0$ (its value is less than 0.1 from approximately $y^* = \pm 1.6$) in agreement with our definition of the effective pore width.

The temperature profiles of the WCA system obtained using Eqs. (12), (13), and (23) are plotted in Fig. 3. The two configurational expressions are in good agreement with the kinetic temperature and give the expected flat profile. If one considers the averages of the various temperatures in the region between $y^* = 1.0$ and $y^* = -1.0$, the temperature T_{con1} yields a deviation of 2.2% from the kinetic temperature, whereas the temperature T_{conf} is in excellent agreement with the kinetic temperature (deviation of 0.05%). Not surprisingly, we observe some discrepancy for the bin closest to the walls; very few atoms are contained in this bin resulting in poor statistics and a reduced reliability for the configurational expressions.

We then ran several simulations with different numbers of fluid particles: (1) to check that the two configurational expressions give the same answer for a large system size, (2) to check that the T_{con1} expression exhibits a $1/N$ dependence on the system size for the WCA potential, and (3) to give an estimate of the error made using the configurational expressions for small systems (and consequently to determine the minimum system size for an accurate configurational temperature). It should also be noted that the importance of the system size issue is enhanced in this kind of application since the configurational expressions are applied in each bin and not on the whole system (i.e., on systems containing an average of 16 atoms between $y^* = -1.5$ and $y^* = 1.5$ for a fluid containing a total number of 288 atoms). We have thus run simulations with 144, 576, and 1152 fluid atoms within the same four atomic diameters wide pore and keeping the

FIG. 4. Variation of temperature values with system size. Temperatures are reported as a fraction of the reduced kinetic temperature for both T_{con1} (open squares) and T_{conF} (open diamonds).

same number of bins. We have then taken the average value of the three expressions for the temperature in the central region (between $y^* = -1.0$ and $y^* = 1.0$). The results are plotted against the inverse total size of the system (which is a multiple of the average number of atoms per bin) in Fig. 4. One can see from this graph that the two configurational expressions and the kinetic temperature give the same answer in the thermodynamic limit and that T_{con1} clearly exhibits a $1/N$ system size dependence. This effect prevents one from using this expression to determine high resolution temperature profiles for a reasonable total number of particles. However, it is shown that T_{conF} can reliably be used for this purpose since it yields an excellent agreement with the kinetic temperature for all system sizes.

In recent work, Jepps *et al.*⁷ have shown that the configurational expressions for the temperature depend on the density of the studied system. Since the density profile of the LJ system exhibits stronger and more numerous oscillations than the WCA system, it is of interest to check that the configurational temperature profiles are also correct for this system. The configurational temperature profiles actually show a little oscillatory behavior partly due to the density dependence of the configurational expressions. However, this phenomenon is also enhanced by the discontinuity of the first and the second derivatives of the LJ potential at the cutoff radius. A LJ potential whose first and second derivatives are continuous can be obtained by truncating the LJ potential at for instance 1.8σ and by fitting a fifth order polynomial function (a fifth order spline) so that the potential function and its first and second derivatives are continuous at 1.8σ and at the cutoff radius. Using the LJ+spline potential has no noticeable effect on the density profile and allows us to slightly reduce (by 25%) the amplitude of the oscillations in the configurational temperature profiles (Fig. 5). We observe mainly the same features as in the case of the WCA fluid: T_{con1} underestimates the temperature by 3% while T_{conF} again performs better and yields a deviation of 0.8% from the kinetic temperature. Both configurational expressions exhibit a little oscillatory behavior correlated with the oscillations in the density profile.

The zeroth law of thermodynamics requires that the temperature of this equilibrium system should be uniform. It is

FIG. 5. Temperature profile for a LJ+spline system using the peculiar kinetic energy (filled circles) or the configurational expressions T_{con1} (open squares) or T_{conF} (open diamonds). The density profile (crosses) for this system is also superimposed.

remarkable that in spite of the finite size and the finite cutoff effects, the amplitude of the oscillations in the configurational temperature profiles in the WCA and in the LJ systems are so weak given the strong oscillations in the density profiles. This is very likely due to a compensation of the contributions from interactions between layers by contributions from in-plane interactions.

V. NEMD SIMULATIONS OF PLANAR POISEUILLE FLOW

The configurational expressions for the temperature are now applied to the calculation of the temperature profile within a confined fluid undergoing planar Poiseuille flow. We first performed NEMD simulations with an external driving force of 0.1 for a WCA and also for a LJ fluid. Simulations of the same systems have been recently performed.³ These simulations will provide a useful test of the NEMD results presented here. We have also performed simulations of a WCA fluid undergoing Poiseuille flow with an applied force of 0.5.

The number density profiles for the three systems studied in this work are plotted in Fig. 6. The profiles obtained with an external force of 0.1 exhibit the same features as the

FIG. 6. Number density profiles for a WCA fluid with an external field of 0.1 (straight line) and of 0.5 (long dashed line) and for a LJ system (dotted line) with an external field of 0.1.

FIG. 7. Scaled streaming velocity profiles obtained from fitting Eq. (22) to the streaming velocity data (same legend as Fig. 6).

results of Travis and Gubbins³ (we note that the peaks close to the walls are slightly higher in our results). The same overall structure as in the equilibrium system is observed. The field acts as a perturbation about the fluid structure induced by the confinement. The maxima in the density profiles close to the walls are reduced slightly and occur at smaller values of $|y^*|$ as a result of the flow. Not surprisingly, this phenomenon is enhanced at higher forces; we observe that increasing the applied force tends to displace atoms from the region near the walls towards the center of the channel where the flow velocity is higher.

Figure 7 shows the scaled streaming velocity profiles obtained by fitting the streaming velocity data for the three systems. The three profiles differ strongly from the quadratic Navier–Stokes profile and require the use of Eq. (22) to be satisfactorily described. Again, good agreement between our results and those reported by Travis and Gubbins³ is obtained. In particular, we observe several extrema in the velocity profile. The presence of extrema in these profiles yield zeros in the strain rate profiles and consequently, discontinuities in the shear viscosity profiles if calculated using a local relationship.³ The oscillations for a WCA fluid are less important than for a LJ fluid and the profile is also flatter around the center of the channel. We also note that the relative amplitude of these oscillations is reduced when the applied force is increased.

FIG. 8. Temperature profiles for from bottom to top, a LJ fluid with an external field of 0.1, a WCA fluid with an external field of 0.1 and of 0.5 (same legend as Fig. 3).

The temperature profiles are plotted in Fig. 8. The kinetic temperature profiles obtained for the WCA and the LJ fluid with an external force of 0.1 are in quantitative agreement with the findings of Travis and Gubbins.³ As observed at equilibrium, the $T_{\text{con}F}$ expression performs better than the $T_{\text{con}1}$ expression and is in excellent agreement with the kinetic temperature in all cases. The discrepancy between the two configurational expressions increases with the intensity of the external force. One can also see that these expressions underestimate the temperature for the two bins closest to the walls for an external force of 0.5. However, at equilibrium and for an external force of 0.1, only the closest bin to the wall is associated with low configurational temperatures. This is due to the fact that the peaks in the density profiles are moved towards the center when the external force is increased, resulting in a less reliable application of the configurational expressions in the two closest bins for an external force of 0.5.

VI. CONCLUSIONS

We have applied two recently derived configurational expressions for the temperature to confined atomic fluids in a slit pore with a width of four molecular diameters. The system has first been divided into bins and the configurational temperatures have been calculated in each of these bins. The temperature profiles so obtained are then compared to the kinetic temperature both at equilibrium and in NEMD simulations of planar Poiseuille flow.

At equilibrium, the two configurational expressions are in good agreement with the kinetic value. We point out that the first-order expression $T_{\text{con}1}$ exhibits a significant dependence on the size of the system. This effect is enhanced by the binning procedure used here to determine the profile. On the other hand, the $T_{\text{con}F}$ expression yields a result in excellent agreement with the kinetic value for all the systems sizes studied.

In nonequilibrium systems, the calculation of the kinetic temperature required the prior determination of the streaming velocity profile. The peculiar kinetic energy and hence the kinetic temperature were then calculated. Again, the results obtained from the $T_{\text{con}F}$ expression were in excellent agreement with the kinetic value.

The application of these configurational expressions to the calculation of temperature profiles of confined molecular fluids seems very promising. In this case, the determination of the streaming velocity cannot be achieved as easily as in the atomic case. The configurational expressions provide a convenient way to overcome this difficulty and might allow one to compute temperature profiles in, for instance, confined lubricants such as alkanes. This will be the topic of future work.

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