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Configurational temperature profile in confined fluids. II. Molecular fluids

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In an earlier paper, we applied configurational expressions of the temperature to the calculation of temperature profiles within a confined atomic fluid. This paper focuses on the application of these expressions to confined molecular fluids using ethane and hexane as examples. We first give configurational expressions for the temperature for these constrained systems. The configurational temperature profiles so obtained are compared to the kinetic temperature calculated using the equipartition principle, in equilibrium systems. These expressions are then used in nonequilibrium molecular dynamics (NEMD) simulations of fluids undergoing planar Poiseuille flow. We show that these configurational expressions provide a direct and accurate determination of the temperature profile for these systems. © 2001 American Institute of Physics. [DOI: 10.1063/1.1356000]

I. INTRODUCTION

Configurational expressions for the temperature have been recently derived.^{1–4} These expressions require only configurational information. They can be used to compute the temperature in Monte Carlo simulations when the particles momenta are undetermined; this expression can therefore provide a useful test of the correct implementation of an NVT or NPT Monte Carlo simulation.² These expressions are of particular interest for a nonequilibrium system. In that case, the temperature is usually calculated by taking averages of the peculiar kinetic energy. In nonequilibrium molecular dynamics (NEMD) simulations of a confined atomic fluid undergoing planar Poiseuille flow, the calculation of the peculiar kinetic energy is achieved through an indirect procedure.^{5–7} The streaming velocity of the fluid is determined by fitting an assumed profile to the streaming velocity data. The peculiar kinetic energies can then be calculated by subtracting the streaming kinetic energy. The accuracy of this procedure relies on the accuracy of fit of the assumed profile fitted to the streaming velocity data. Every deviation of the fitted profile for the actual profile will yield inaccurate—and hotter—temperatures. The assumed profile must therefore be flexible enough to account for the deviations from the Navier–Stokes profile due to the confining walls. In a preceding paper,⁸ we have shown that using a configurational expression for the temperature provides a reliable and a more direct way to determine a temperature profile.

It is however even more difficult to determine a kinetic temperature for nonequilibrium molecular systems. Let us consider the example a rigid diatomic molecule undergoing planar Poiseuille flow. In addition to the translational streaming velocity of the center of mass, one has also to take into account the shear induced molecular rotation.⁹ The kinetic temperature so determined becomes however less and less accurate since it is now required to also fit the angular velocity profile.⁹ Moreover, it is unclear how one can extend this procedure to the study of the flow of longer and flexible molecules.

The aim of this paper is to apply configurational expres-

sions of the temperature to the study of confined molecular fluids. Semiflexible models with bonding and possibly bond-bending constraints are often used to describe molecules such as alkanes.¹⁰ Following Lue and Evans¹¹ and in line with a precedent paper,⁸ we propose in this work two different expressions for the configurational temperature for systems with constraints. In the first place, these expressions are tested against equilibrium molecular dynamics simulations of confined ethane and hexane. In both cases, the kinetic temperature profile is compared with the two configurational temperature profiles. We then perform NEMD simulations of ethane and hexane undergoing planar Poiseuille flow. The configurational temperature profiles are computed in each case. In the case of ethane, we investigate the effect on the kinetic temperature profile of neglecting the shear induced molecular rotation and the oscillations in the translational streaming velocity profile due to the confining walls.

II. CONFIGURATIONAL EXPRESSIONS FOR THE TEMPERATURE

A. General expressions for constrained systems

Let us consider an N -molecule system. We denote a phase space vector by $\Gamma \equiv (\dots, \mathbf{q}_{i\alpha}, \dots, \mathbf{p}_{i\alpha}, \dots)$ where $\mathbf{q}_{i\alpha}$ is the position coordinate of atom α of molecule i and $\mathbf{p}_{i\alpha}$ its momentum. In a more general way, one can define $\Gamma = \{\Gamma_{i\alpha a}\}$, where a is either a position coordinate ($a = 1, 2, 3$) or a momentum component ($a = 4, 5, 6$) of atom α of molecule i . Each molecule is submitted to a set of K holonomic constraints of the general form,

$$C_n(\Gamma) = 0 \quad \text{for } n = 1, \dots, K. \quad (1)$$

We now define a microcanonical (NVE) ensemble for a given Hamiltonian $H(\Gamma) (= K(\dots, \mathbf{p}_{i\alpha}, \dots) + V(\dots, \mathbf{q}_{i\alpha}, \dots))$ 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

$$S(E) = k_B \ln(V_r(N, V, E)) = k_B \ln \int_{\mu C(E)} d\Gamma. \quad (2)$$

The thermodynamic temperature is obtained through the following differentiation:

$$\frac{1}{T} = \left. \frac{\partial S}{\partial E} \right|_V. \quad (3)$$

Let us displace the phase points Γ of the (NVE) ensemble to the points Γ' along the phase space gradient of the Hamiltonian,

$$\Gamma'(\Gamma) = \Gamma + \mathbf{n}(\Gamma) \Delta E = \Delta + \frac{\mathbf{G} \cdot \nabla H(\Gamma)}{\nabla H(\Gamma) \cdot \mathbf{G} \cdot \nabla H(\Gamma)} \Delta E, \quad (4)$$

where ΔE stands for a change in energy of the system.

$\mathbf{G}$ is a fairly arbitrary matrix.⁴ We must however ensure that

$$\nabla H(\Gamma) \cdot \mathbf{G} \cdot \nabla H(\Gamma) \neq 0, \quad (5)$$

and that the $n = 1, \dots, K$ constraints are still satisfied at the new phase points Γ' ,¹¹

$$C_n(\Gamma') = C_n(\Gamma) + \Delta E \cdot \nabla C_n(\Gamma) \cdot \mathbf{n}(\Gamma) = 0. \quad (6)$$

This can be done by choosing the matrix $\mathbf{G}$ such that, for each n ,

$$\nabla C_n(\Gamma) \cdot \mathbf{G} \cdot \nabla H(\Gamma) = 0. \quad (7)$$

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

$$S(E + \Delta E) = k_B \ln \int_{\mu C(E + \Delta E)} d\Gamma = k_B \ln \int_{\mu C(E)} J(\Gamma) d\Gamma, \quad (8)$$

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

$$J(\Gamma) = \left| \frac{\partial \Gamma'(\Gamma)}{\partial \Gamma} \right| = 1 + \nabla \cdot \mathbf{n}(\Gamma) \Delta E. \quad (9)$$

Therefore, introducing Eqs. (8) and (9) in Eq. (2), we obtain the following expression for the temperature:

$$\frac{1}{T} = \left. \frac{\partial S}{\partial E} \right|_V = k_B \langle \nabla \cdot \mathbf{n} \rangle_E. \quad (10)$$

It has been shown that this expression holds for the microcanonical and the canonical ensembles.⁴

We now have to choose the elements of matrix $\mathbf{G}$ such that the constraints are satisfied. The elements of this matrix are defined with six subscripts: $g_{i\alpha a, j\alpha' b}$, where a (respectively b) is a coordinate [position coordinate if $a \leq 3$ (resp. $b \leq 3$) or momentum if $a > 3$ (resp. $b > 3$)] of atom α (resp. α') of molecule i (resp. j). If we choose $g_{i\alpha a, j\alpha' b} = \delta_{ij} \delta_{ab}$ if a and b refers to position coordinates (a and $b \leq 3$) and 0 otherwise, we have

$$\begin{aligned} & \sum_{i\alpha a, j\alpha' b} [\partial_{i\alpha a} C_n(\Gamma)] g_{i\alpha a, j\alpha' b} [\partial_{j\alpha' b} H(\Gamma)] \\ &= \sum_i \left(\sum_a \frac{\partial C_n(\Gamma)}{\partial \mathbf{r}_{i\alpha}} \right) \left(\sum_{\alpha'} \frac{\partial H(\Gamma)}{\partial \mathbf{r}_{i\alpha'}} \right) = 0, \end{aligned} \quad (11)$$

since for all constraints n , one has

$$\sum_{\alpha} \frac{\partial C_n(\Gamma)}{\partial \mathbf{r}_{i\alpha}} = 0. \quad (12)$$

Equation (10) therefore reduces to

$$\frac{1}{k_B T} = \sum_i \sum_{(\alpha, \alpha') \in i} \left\langle \frac{\partial}{\partial \mathbf{r}_{i\alpha}} \cdot \left[\frac{1}{\Delta} \frac{\partial H}{\partial \mathbf{r}_{i\alpha'}} \right] \right\rangle, \quad (13)$$

where

$$\Delta = \sum_i \sum_{(\alpha, \alpha') \in i} \frac{\partial H}{\partial \mathbf{r}_{i\alpha}} \cdot \frac{\partial H}{\partial \mathbf{r}_{i\alpha'}}. \quad (14)$$

The first order configurational expression^{4,8,11} can thus be written as

$$\frac{1}{k_B T_{\text{conf}}} = \sum_i \sum_{(\alpha, \alpha') \in i} \left\langle \frac{1}{\Delta} \frac{\partial}{\partial \mathbf{r}_{i\alpha}} \cdot \frac{\partial H}{\partial \mathbf{r}_{i\alpha'}} \right\rangle. \quad (15)$$

Jepps *et al.*⁴ have recently provided a more general expression of Rugh's theorem,

$$\frac{1}{T} = k_B \frac{\langle \nabla \cdot \mathbf{B}(\Gamma) \rangle}{\langle \nabla H \cdot \mathbf{B}(\Gamma) \rangle}, \quad (16)$$

where $\mathbf{B}(\Gamma)$ is an arbitrary phase space vector field. This expression holds for the microcanonical and the canonical ensemble.⁴ 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),

$$\frac{1}{k_B T_{\text{conf}}} = \frac{\left\langle \sum_i \sum_{(\alpha, \alpha') \in i} \frac{\partial}{\partial \mathbf{r}_{i\alpha}} \cdot \frac{\partial H}{\partial \mathbf{r}_{i\alpha'}} \right\rangle}{\langle \sum_i \sum_{(\alpha, \alpha') \in i} \Delta \rangle}. \quad (17)$$

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 for instance of interest to calculate the temperature along the direction of confinement. We use the fact that the matrix $\mathbf{G}$ is arbitrary for this purpose.

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 $g_{i\alpha a, j\alpha' b} = \delta_{ij} \delta_{ab} \delta_{i\text{bin}} \delta_{j\text{bin}}$ ($\delta_{i\text{bin}}$ is equal to 1 if the center of mass of molecule i is located into bin) and 0 otherwise, we obtain for the first order configurational temperature,

$$\frac{1}{k_B T_{\text{conf}}(\text{bin})} = \sum_{i \in \text{bin}} \sum_{(\alpha, \alpha') \in i} \left\langle \frac{1}{\Delta_{\text{bin}}} \frac{\partial}{\partial \mathbf{r}_{i\alpha}} \cdot \frac{\partial H}{\partial \mathbf{r}_{i\alpha'}} \right\rangle, \quad (18)$$

and the configurational temperature, as expressed in Eq. (17), is evaluated as

$$\frac{1}{k_B T_{\text{conf}}(\text{bin})} = \frac{\left\langle \sum_{i \in \text{bin}} \sum_{(\alpha, \alpha') \in i} \frac{\partial}{\partial \mathbf{r}_{i\alpha}} \cdot \frac{\partial H}{\partial \mathbf{r}_{i\alpha'}} \right\rangle}{\langle \sum_{i \in \text{bin}} \sum_{(\alpha, \alpha') \in i} \Delta_{\text{bin}} \rangle}, \quad (19)$$

where

FIG. 1. Equilibrium temperature profile for ethane using the peculiar kinetic energy (filled circles) or the configurational expressions $T_{\text{con}i}$ (open squares) or $T_{\text{con}F}$ (open diamonds).

$$\Delta_{\text{bin}} = \sum_{i \in \text{bin}} \sum_{(\alpha, \alpha') \in i} \frac{\partial H}{\partial \mathbf{r}_{i\alpha}} \cdot \frac{\partial H}{\partial \mathbf{r}_{i\alpha'}}. \quad (20)$$

We note that this is one way to compute a configurational temperature profile. There are of course many other possible ways since the matrix $\mathbf{G}$ is arbitrary. We also add that, using this property of matrix $\mathbf{G}$, it is possible to derive configurational expressions for any kind of geometry.

III. METHOD

A. Models

Alkane molecules are modeled by a chain of identical sites or united atoms representing CH_2 or CH_3 groups. The united atoms and the wall atoms are modeled by the same truncated and shifted Lennard-Jones potential, often referred as the WCA potential. United atoms from different molecules, united atoms more than three bonds apart on the same molecule, and wall atoms interact through the following formula:

$$u(r_{ij}) = -4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^6 - \left(\frac{\sigma}{r_{ij}} \right)^{12} \right] + \epsilon \quad r \leq r_c, \\ u(r_{ij}) = 0 \quad r > r_c, \quad (21)$$

where r_{ij} is the distance between atom i and atom j , $r_c = 2^{1/6}\sigma$ 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. Since it is truncated at its minimum, the WCA potential is purely repulsive.

The bond length is fixed to 0.39σ and the bond angles are fixed at 109.47° . The bond angle is constrained using a next-nearest neighbor distance constraint.¹² A torsional potential that depends on the dihedral angle ϕ acts between each pair of methyl and methylene groups that are three bonds apart on a given alkane chain. Following Ryckaert and Bellemans,¹⁰ we use a truncated power series in the cosine of ϕ for this torsional potential,

$$u_{\text{tors}} = \sum_{i=0}^5 a_i \cos^i \phi. \quad (22)$$

The values of coefficient $\{a_i\}$ are given by $\{15.5, 20.31, -21.92, -5.1, 43.83, -52.61\}$.

B. Simulation technique

The simulation technique is the same as the one described in the first paper of the series.⁸ We therefore briefly outline how the simulations were carried out. 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 forces, with a spring constant set to 150.15, and a constraint mechanism, based on Gauss' principle of least constraint,¹² 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.¹²

The pore width (PW) is chosen to be equal to 10.2σ . Simulations were performed on systems containing 360 molecules of ethane and 240 molecules of hexane. There is no unambiguous definition for the volume accessible to the fluid.⁵⁻⁷ In line with previous work,¹¹ we choose to define the effective pore width as $\text{PW}_{\text{eff}} = 9.0\sigma$. Simulations are thus performed at a reduced atomic density of 0.68 for ethane and of 1.36 for hexane. The fluid atoms obey Newton's equation of motion,

$$\dot{\mathbf{r}}_{i\alpha} = \frac{\mathbf{p}_{i\alpha}}{m}, \quad (23a)$$

$$\dot{\mathbf{p}}_{i\alpha} = \mathbf{F}_{i\alpha}^{\text{WCA}} + \mathbf{F}_{i\alpha}^{\text{C}} + \mathbf{iF}_e, \quad (23b)$$

where $\mathbf{F}_{i\alpha}^{\text{WCA}}$ is the force acting on the united atom α of molecule i due to both fluid–fluid and wall–fluid interatomic interactions, $\mathbf{F}_{i\alpha}^{\text{C}}$ is the force due to bonding and bond-bending constraints, and $\mathbf{iF}_e$ is the external force used to drive the Poiseuille flow along the x axis. Constraint forces are determined using Gauss' principle of least constraints.¹² The parentheses indicate that the external field is only switched on 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).

C. Calculation of density and temperature profiles

We used the method of planes to calculate the density profiles and the streaming velocity profile.¹³ The temperature profiles for the kinetic and configurational expressions were computed by dividing the channel into bins along the y axis and estimating the temperature in each bin for each expression. The simulation cell is divided along the y axis into a number (200 in this work) of equally spaced planes of A

$=L_x \times L_z$ area. The atomic density can then be evaluated at the planes positions according to the following formula:

$$\bar{n}(y) = \lim_{\tau \rightarrow \infty} \frac{1}{\tau A} \sum_i \sum_{0 < t_{cr(i)} < \tau} \frac{M}{|\dot{y}_{com-i}(t_{cr(i)})|}, \quad (24)$$

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

In NEMD simulations, the calculation of the kinetic temperature requires computing the averages of the peculiar kinetic energy. As stated earlier, the determination of the streaming velocity is difficult for molecular fluids. Travis and Evans have shown how to determine the angular and the translational streaming velocity for a diatomic molecule.⁹ However, it is unclear how one can extend this procedure to a longer and flexible molecule like hexane. We have chosen here to only determine the translational streaming velocity and to calculate the peculiar momenta and hence the peculiar kinetic energy by subtraction of this translational streaming velocity. This procedure will allow us to give an estimate of the effect of neglecting the shear induced rotation in the calculation of the temperature. Moreover, as the angular velocity is equal to zero at the center of the pore,⁹ the value obtained by this procedure should be correct at $y^*=0$. This will provide a useful test of the results given by the configurational expressions at this point.

We proceed as follows. We first evaluate the momentum density at the planes positions,

$$\bar{J}_x(y) = \lim_{\tau \rightarrow \infty} \frac{1}{\tau A} \sum_i \sum_{0 < t_{cr(i)} < \tau} \frac{m \dot{x}_{com-i}(t_{cr(i)})}{|\dot{y}_{com-i}(t_{cr(i)})|}, \quad (25)$$

where $\bar{J}_x(y)$ is the average momentum density at y and $\dot{x}_{com-i}$ is the x component of the velocity of the center of mass of molecule i .

The average streaming velocity is obtained through its definition,

$$\bar{u}_x(y) = \frac{\bar{J}_x(y)}{\bar{n}(y)}. \quad (26)$$

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,^{6,7}

$$\bar{u}_x(y) = a_0 + a_1 y^2 + \sum_{n \geq 2} a_n \cos\left(\frac{2\pi(n-1)y}{PW_{eff}}\right), \quad (27)$$

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 (it would be of course possible to compute the kinetic temperature from the methods of plane but we chose to use a bins method for the three types of temperature profiles).

The kinetic temperature is given by

FIG. 2. Equilibrium temperature profile for hexane (same legend as in Fig. 1).

$$T_{kin}(\text{bin}) = \frac{\langle \sum_{i=1}^{N_{bin}} m [\mathbf{v}_i - \bar{\mathbf{u}}_x(y_i)] [\mathbf{v}_i - \bar{\mathbf{u}}_x(y_i)] \rangle}{\langle 3N_{bin} \rangle}. \quad (28)$$

Because separate simulations runs are used to determine $\bar{u}_x(y)$ and $T_{kin}(y)$, we do not have to reduce the number of degrees of freedom from $3N_{bin}$ in Eq. (28). We also compute the configurational temperatures given by Eqs. (18) and (19).

The initial configurations were created by placing the centers of mass of each fluid molecule at lattice points between the two solid walls. The size of each united atom was then grown from an initial nearly zero size to full size in ten thousand time steps. The configurations so obtained were then equilibrated 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 two million time steps in both equilibrium and NEMD simulations with a reduced time step of 0.001.

IV. EQUILIBRIUM SIMULATIONS

In the first place, we have tested the configurational expressions for the temperature given in Sec. II against equilibrium molecular dynamics simulations of confined ethane and hexane. The temperature profiles obtained using Eqs. (18), (19), and (28) are plotted in Figs. 1 and 2 for ethane and hexane, respectively. For both molecules, the two configurational expressions are in good agreement with the kinetic value and give the expected profile. In both cases, the T_{conf} expression is in excellent agreement with the kinetic temperature (deviation of 0.2% for ethane and of 0.4% for hexane). The temperature T_{con1} yields higher deviations from the kinetic values (deviation of 7.4% for ethane and of 3.8% for hexane). This is due to finite size effects in the first order expression T_{con1} as reported in the first paper of this series.⁸ It should also be kept in mind that the confined ethane system has been simulated at a lower density yielding a stronger deviation than in the case of hexane. This phenomenon is enhanced by the procedure used in this work;⁸ the first order configurational expression is computed for each bin and therefore is applied on few molecules.

FIG. 3. Atomic density profiles for confined ethane (dotted line) and for hexane (straight line) for $F_e=0.5$.

V. NEMD SIMULATIONS OF PLANAR POISEUILLE FLOW

The configurational expressions of the temperature are now applied to the calculation of the temperature profile within confined ethane and hexane undergoing planar Poiseuille flow. In both cases, we have performed NEMD simulations with an external driving force of 0.5.

The mass density profiles for the two systems studied in this work are plotted in Fig. 3. Both profiles fall to zero at approximately $y^* = \pm 4.5$ suggesting an effective pore width of 9.0σ . They also exhibit strong oscillations near the wall associated with formation of layers in the pore. These profiles are in qualitative agreement with those obtained by Travis and Evans⁹ for a diatomic fluid.

Figure 4 shows the translational streaming velocity profiles obtained by fitting either a quadratic profile or Eq. (27) to the streaming velocity data for confined ethane. We note that, the velocity profile exhibits a quadratic behavior in the central region. However, a purely quadratic profile is unable to correctly describe the sharp drop to zero of the velocity profile. This sharp drop may be accounted by the fact that the wall molecules differ from the fluid molecules.⁹ Overall, our findings are in good agreement with the findings of Travis and Evans.⁹ The translational streaming velocity profiles obtained by fitting Eq. (27) to the streaming velocity data for

FIG. 4. Streaming velocity profile for confined ethane: filled circles are simulation data, the dotted line is the Navier–Stokes parabolic fit, and the straight line is the parabolic+cosine Fourier series fit to the simulation data.

FIG. 5. Streaming velocity profile for confined hexane: filled circles are simulation data and the straight line is the parabolic+cosine Fourier series fit to the simulation data.

confined hexane is plotted in Fig. 5. This profile exhibits the same qualitative features as the one plotted in Fig. 4. As for hexane, a quadratic behavior in the central region, shoulders between $y^* = \pm 3.5$ and $y^* = \pm 4$ and a sharp drop to zero at approximately $y^* = \pm 4.5$ are observed. Again, we observe that a narrow confinement and possibly the difference of type of molecules between the walls and the fluid yield a strong deviation from the Navier–Stokes quadratic profile close to the walls.

The temperature profile for confined ethane is plotted in Fig. 6. As observed in the case of a confined atomic fluid,⁸ the finite size effects are enhanced in nonequilibrium systems for the T_{conI} expression and the results obtained using this formula clearly underestimate the temperature. In the central region of the pore, there is an excellent agreement between the values computed from the kinetic expression using either a purely quadratic function or Eq. (27) to describe the translational streaming velocity profile and from the T_{conF} expression. Such an agreement was expected in this region. The translational streaming velocity profile is well described by both functional fits in the central region and therefore, the two values obtained for the kinetic temperature should match. Moreover, as shown by Travis and Evans⁹ in the case of a diatomic fluid, the angular streaming velocity is

FIG. 6. Temperature profiles for confined ethane for $F_e=0.5$ using the peculiar kinetic energy obtained from a parabolic fit to the streaming velocity (filled triangles) and a parabolic+cosine Fourier series fit (straight line) or the configurational expressions T_{conI} (open squares) or T_{conF} (open diamonds).

FIG. 7. Temperature profiles for confined hexane for $F_e=0.5$ using the peculiar kinetic energy obtained from a parabolic+cosine Fourier series fit to the streaming velocity (straight line) or the configurational expressions T_{con1} (open squares) or T_{conF} (open diamonds).

equal to zero at $y^*=0$. The peculiar kinetic energy at $y^*=0$ is thus exactly obtained by subtracting the translational streaming velocity. It is therefore expected that the T_{conF} expression yields the same value at $y^*=0$ as the two ways of computing the kinetic temperature used in this work. There are however several discrepancies between these three temperature profiles close to the walls. First, using a purely quadratic profile to fit the streaming velocity data yields hotter temperatures than when Eq. (27) is used. This is because the quadratic profile is unable to describe the sharp drop in the velocity profile. Secondly, even when using the functional fit of Eq. (27), we obtain a value which is higher than the one given by the T_{conF} expression. This may result from the neglect of the angular streaming velocity which reaches its highest values close to the walls.

The temperature profile for confined hexane is plotted in Fig. 7. The results obtained for hexane confirm our findings on the confined ethane system: (1) the T_{con1} expression underestimate the temperature and (2) while there is a good agreement in the central region of the pore between the kinetic temperature and the value obtained from the T_{conF} expression, the kinetic temperature is hotter close to the walls.

VI. CONCLUSIONS

We have applied two configurational expressions for the temperature to confined molecular fluids in a slit pore at an effective width of nine molecular diameters. In each case, 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, for both systems, the two configurational expressions are in good agreement with the kinetic value. As observed for atomic fluids,⁸ the first-order expression T_{con1} 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_{conF} 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 requires the prior determination of the streaming velocity profile. Whereas the streaming velocity profile of atoms or of the centers of mass of molecules (i.e., the translational streaming velocity profiles of the molecular fluid) can be easily calculated, its complete determination is particularly difficult to achieve for molecular fluids. However, the configurational expressions require only configurational information. They can therefore be used to circumvent these difficulties. For both confined ethane and hexane, the results obtained the T_{conF} expression were in excellent agreement with the kinetic value at the center of the pore where the shear induced molecular rotation is negligible. This result is a strong evidence of the reliability of the T_{conF} expression to lead correct value for the temperature in such systems. We were also able to show that neglecting the shear induced molecular rotation or using a Navier–Stokes quadratic profile to describe the translational streaming velocity profile yielded overestimations of the temperature close to the walls.

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