Nonequilibrium Molecular Dynamics Simulations of Coupled Heat- and Mass Transport in Binary Fluid Mixtures in Pores[1]

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ABSTRACT

Molecular dynamics simulations were carried out for a binary fluid mixture in a slit pore. The fluid was an argon-like Lennard-Jones/spline model. The pore wall was represented by the Steele model for a layered graphite structure. The pore had a heat source in one end and a heat sink in the other, resulting in a lateral temperature gradient, a Soret effect, and a thermal creep flow along the pore wall. Potential models with various depths were used to examine the effect of wetting and adsorption on the thermal creep flow.

The main results were: (1) A relatively strong creep flow was generated parallel to the wall by the temperature gradient. For strongly attracting fluid-wall potentials, the flow occurred from the cold to the hot end of the pore near the wall (except for the very narrow pore), and opposite in the center of the pore. For a purely repulsive potential, the flow was weak and mostly in the opposite direction. (2) The thermal diffusion coefficient was comparable to that in bulk fluid at the same overall density, except when the creep flow was strong, in which case the thermal diffusion was blurred by the convective mixing.

KEY WORDS: microporous; nonequilibrium molecular dynamics; slit pore; surface tension; thermal creep; thermal diffusion.

1. INTRODUCTION

In a porous system, it is well known that the thermodynamic properties, such as the phase behavior, may deviate very much from the properties of the bulk fluid. Much less is known about the transport properties, and in particular about coupled transport processes such as coupled heat- and mass transport. Thermal creep flow may, however, play a role when normal convection is lacking (under zero gravity), when the system has been established over a long time (hydrocarbon reservoirs subject to the geothermal gradient), or when the thermal force is extremely large.

In most cases, it is very difficult to describe thermal creep, and for that matter almost any transport process, in a porous material due to the complexity of the pore structure. Most studies based on computer simulations have therefore been made for a pore model with simple geometry, notably for slit pores [1]. The studies of transport phenomena include diffusion, which depends only on the fluid particles and the fluid-wall interactions [1]. Thermal conduction depends in addition on the matrix, and is therefore a more difficult problem, both from a phenomenological and a computational point of view. In this paper, we study thermal diffusion (the Soret effect), i.e. the diffusive process driven by a temperature gradient in a slit pore by nonequilibrium molecular dynamics (NEMD) simulations, and it turns out that this study is feasible and illustrating for very small pores (less than 10 nm pore width).

The boundary-driven NEMD technique has proved to be an accurate and effective method to determine the "cross-coefficients" in coupled transport processes, such as the Soret and Dufour coefficients in coupled heat- and mass transport [2,3]. Several studies have been carried out for thermal diffusion, in particular for isotope mixtures, and we now begin to understand at least the sign of the effect, i.e. which of the components will be driven toward the hot side of the system for a given temperature gradient.

This paper describes a study on a model of Lennard-Jones/spline (LJ/s) particles in a slit pore where the pore width and the interaction between the fluid particles and the wall are the main variables. The details of the model and simulation conditions are given in

section 2. Section 3 describes how the thermal diffusion factor and the mass fluxes in the pore depend on these variables. A possible explanation of the thermal creep flow is given in terms of the fluid-wall interfacial tension.

2. MODEL AND SIMULATION CONDITIONS

2.1. Simulation cell and potential models

The simulations were carried out in a non-cubic simulation cell with walls at the top and bottom (perpendicular to the *z*-axis). The general layout of the simulation cell is shown in Fig. 1. The cell was divided into 200 control volumes that extended over the entire MD cell in *y*-direction and was organized as 20×10 or 10×20 in *x*×*y*-directions; the widest pore had the highest number of layers in *z*-direction. The system was thermostatted locally in regions at each end of the cell, marked "H" and "C" in the figure, creating a temperature gradient in the *x*-direction.

The fluid-fluid and fluid-wall interactions were modeled with the LJ/s potential [4] and the Steele 10-4-3 (10-4-3) potential [5], respectively. The LJ/s potential is defined by

$$\phi_{ij}(r) = \begin{cases} 4\epsilon_{ij}\left[\left(\dfrac{\sigma_{ij}}{r}\right)^{12} - \left(\dfrac{\sigma_{ij}}{r}\right)^{6}\right] & \text{for } r \le r_s \\ a_{ij}(r-r_c)^2 + b_{ij}(r-r_c)^3 & \text{for } r_s \le r \le r_c \\ 0 & \text{for } r \ge r_c \end{cases} \tag{1}$$

where $r_s = (26/7)^{1/6}\sigma_{ij}$, $r_c = (67/48)r_s$, $a_{ij} = -(24192/3211)\varepsilon_{ij}/r_s^2$, and $b_{ij} = -(387072/61009)\varepsilon_{ij}/r_s^3$. The parameters σ_{ij} and ε_{ij} represent the molecular diameters and intermolecular potential depths, respectively. The 10-4-3 potential is defined by

$$\phi_{sf}(z) = 2\pi\rho_s\epsilon_{sf}\sigma_{sf}^2\Delta\left[\frac{2}{5}\left(\frac{\sigma_{sf}}{z}\right)^{10} - \left(\frac{\sigma_{sf}}{z}\right)^{4} - \frac{\sigma_{sf}^4}{3\Delta(0.61\Delta + z)^3}\right] \tag{2}$$

where ρ_s is the particle density of the graphite lattice, ϵ_{sf} and σ_{sf} are the potential parameters equivalent to the Lennard-Jones potential, Δ is the distance between graphite layers, and *z* is the fluid-wall distance. Also used was a wall interacting with the fluid

through the repulsive WCA modification of the 10-4-3 potential, i.e. the 10-4-3 potential shifted upwards with the potential depth and truncated at the minimum.

Since the 10-4-3 potential is a function of wall distance only, the particle velocities parallel to the wall (the *x*- and *y*-components) would be unaffected by collisions with the wall. This corresponds to a system with perfect slip conditions. To reduce the effects of perfect slip and to include the effects of a thermostatted wall, the method of diffuse fluid-wall collisions [1] was used as follows: The system was monitored for fluid-wall collisions. When a collision between a fluid particle and the wall was detected as a change in sign of the *z*-component of the particle velocity, the particle was given new velocity components in the *x*- and *y*-directions, drawn from a Maxwell-Boltzmann distribution corresponding to the local wall temperature. The *z*-component was given by the unperturbed equations of motion.

2.2. Simulation conditions

Four different pore widths were studied, 2.5, 3.5, 5.1, and 20.0 molecular diameters. The fluid-fluid interaction parameters were argon-like, and the fluid-wall interaction was modeled with the cross parameters of argon and carbon. In addition, the fluid-wall interaction strength was reduced to ~30 % and ~14 % of the full value. The reduction of the interaction strength was done to reduce the adsorption and make a softer wall repulsion. The simulation conditions are given in terms of the potential parameters in Table I.

The full 10-4-3 fluid-wall attraction at the potential minimum is stronger than the fluid-fluid interaction by a factor between 9 and 12, depending on the pore width. The smaller pores exhibit a deeper potential minimum due to increasing influence from the opposite wall.

The simulations were run between 1.2×10^6 and 1.8×10^6 time steps, out of which the last 1.0 - 1.6×10^6 time steps were used for analysis, leaving 0.2×10^6 time steps for a

steady state to be established. The analysis of the NEMD data was based on accumulated data dumped every 50,000 or 60,000 time step, depending on the system.

3. RESULTS

3.1. Concentration gradients and thermal diffusion factors

During the initial simulation period, in which a steady state was established with a given temperature gradient, the thermal diffusion created a stable concentration gradient. From these gradients we calculated the thermal diffusion factor, defined by

$$\alpha_{12} = -\frac{T\,\nabla x_1}{x_1 x_2\,\nabla T} \tag{3}$$

where x_1 and x_2 are the molar fractions of species 1 and 2, respectively. From Table II, it is seen that the thermal diffusion factor varies both as function of pore size and potential. The very low α_{12} seen for the widest pore is somewhat surprising, given that one expects the value of α_{12} to approach bulk value, ~ 1.0, when the pore width increases. The high α_{12} values seen for the smaller pores is partly explained by the high actual densities of these pores. The low value of α_{12} in the wide pore is explained by the mixing that occurs most strongly in this pore.

3.2. Mass flux

The simulation cell is closed at each end, and the net mass flux in the *x*-direction has to be equal to zero. This does not prevent significant internal mass fluxes local to parts of the cell. When the mass flux in the *x*-direction, parallel to the heat flux, is plotted as a function of *z*, some characteristic flow patterns appear. This flow is best seen in the pores of width 5.1σ and 20σ, and these are shown as examples in Figs. 2 and 3. A negative flux in these figures signifies a mass flux from cold to hot, or from right to left in Fig. 1.

The two-dimensional projection of the flow vectors for the pore of width 20σ in Fig. 4, shows the flow even more clearly. This flow pattern explains the low α_{12} for the 20σ

and 5.1s pores as shown in Table II, as it inhibits the formation of a large concentration gradient. It also explains why a_{12} is lowest for the full potential, as the flow is largest here.

3.3 Surface tension

The driving force behind the observed eddies within the systems is most likely to be the interaction of the fluid particles with the wall, in combination with the temperature gradient. It is known that a gradient in surface tension will cause a mass flow, the so-called Marangoni effect. The fluid-wall interfacial tension gradient, ∇g_{sf}, was computed and is given in Table III along with the significant wall mass flux.

The term "significant wall mass flux" shall be explained further, as determining the direction of the mass flux along the wall is not always a simple task, and the problems and sorting criteria shall be explained. The wall is used as reference because the driving force of the flow is the fluid-wall interfacial tension, which works close (and parallel) to the wall.

If the eddy is small and shifted slightly to one of the walls in the smaller pores (which was observed in some cases), the central counterflow may virtually cancel the wall flow at this wall due to viscous forces. Another problem is that in cases of small mass fluxes, sometimes only the colder part sustains a symmetric flow pattern, while the hot part exhibits chaotic flow that masks the effect of the eddies in the analysis. A third problem is that the diffuse wall condition will assign velocities centered around zero mass flux, reducing even further, already small mass fluxes. The control volumes nearest to the wall in the narrowest pore was influenced by this, as appears in Fig. 2. The term "significant wall mass flux" is used for the mass flux that clearly shows an eddy. A visual inspection of the flow vectors like those in Fig. 4, can determine if for example the hot part has a chaotic pattern that masks the flow pattern of the cold part in the analysis.

We expect that using a corresponding system with specular wall conditions would more clearly (but less realistically) show the thermal creep flow.

4. CONCLUSIONS

We have shown that the fluid-wall interaction generates two eddy currents in a closed pore when the pore is subject to a longitudinal temperature gradient. The flow occurs in the direction from low to high interfacial tension, which is from cold to hot in most of the cases studied here. In the larger pores with purely repulsive fluid-wall interactions, the flow occurs from hot to cold near the wall, but this is also from low to high interfacial tension. The effect is therefore characterized as a thermal Marangoni effect.

The thermal diffusion factor is of the same order of magnitude in the slit pore as in bulk fluid, but the component separation due to thermal diffusion is blurred in the cases with strong eddy currents.

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Table I. Potential parameters and simulation conditions

Quantity	Symbol	Value
Molecular size parameter[1]	σ	0.341 nm
Potential well-depth parameter[1]	ϵ/k_B	118.9 K
Fluid-wall size parameter	σ_{sf}	0.3405 nm
Fluid-wall potential well-depth parameter	ϵ_{sf}/k_B	57.9 K
Reduced fluid-wall potential well-depth parameter #1	ϵ_{sf}/k_B	17.9 K
Reduced fluid-wall potential well-depth parameter #2	ϵ_{sf}/k_B	7.9 K
Density of C atoms in wall	ρ_s	114 /nm^3
Separation of graphite layers	Δ	0.335 nm
Component mass ratio	m_1/m_2	10
Overall fluid density[2]	ρ	10 /nm^3
Temperature at hot pore end, thermostat set point	T_H	240 K
Temperature at cold pore end, thermostat set point	T_C	120 K

[1] The two fluid components had the same values for σ and ϵ and differed only by mass.

[2] This value is nominal based on the wall position. The actual particle number density in the pore is higher, especially for the narrow pores, due to the excluded volume near the walls.

Table II. The thermal diffusion factor α_{12}, at T = 180 K for ρ = 10 /nm^3 and diffuse walls.

		10-4-3	WCA
Pore width	Pot. param.[1]	α_{12}	α_{12}
	Full	1.5 ± 0.1	1.6 ± 0.1
2.5σ	Reduced #1	1.8 ± 0.2	1.7 ± 0.3
	Reduced #2	1.5 ± 0.2	1.9 ± 0.2
	Full	1.0 ± 0.1	1.5 ± 0.1
3.5σ	Reduced #1	1.6 ± 0.1	1.8 ± 0.1
	Reduced #2	1.6 ± 0.1	1.7 ± 0.1
	Full	0.8 ± 0.1	1.5 ± 0.1
5.1σ	Reduced #1	1.5 ± 0.1	1.5 ± 0.1
	Reduced #2	1.5 ± 0.1	1.5 ± 0.1
	Full	0.0 ± 0.1	0.3 ± 0.1
20.0σ	Reduced #1	0.4 ± 0.1	
	Reduced #2	0.4 ± 0.1	

[1] The potential parameters refer to the potential parameters given in Table I for the wall-fluid interaction. The WCA is constructed from the corresponding 10-4-3 potential as described in the text.

Table III. Surface tension gradients and significant wall mass flux.

Pore	e_{sf}/k_B[1]	10-4-3 Potential		WCA Potential	
		∇g (10^6 Nm^{-2})	J_M(10^3 mol/m^{2}s)[2]	$\nabla\gamma^*$ (10^6 Nm^{-2})	J_M(10^3 mol/m^{2}s)[2]
	Full	4.4 ± 0.1	20 ± 3	3.6 ± 0.1	15 ± 2
2.5s	Reduced #1	6.4 ± 0.2	16 ± 3	6.5 ± 0.2	16 ± 3
	Reduced #2	8.4 ± 0.2	11 ± 3	8.5 ± 0.2	11 ± 3
	Full	-6.9 ± 0.1	-7.7 ± 0.3	-1.32 ± 0.05	not significant
3.5s	Reduced #1	-1.1 ± 0.05	not significant	-0.15 ± 0.05	not significant
	Reduced #2	0.6 ± 0.1	not significant	0.68 ± 0.05	not significant
	Full	-7.4 ± 0.1	-30 ± 1	1.05 ± 0.+5	5.47 ± 0.08
5.1s	Reduced #1	-1.33 ± 0.05	-4 ± 1	0.88 ± 0.+5	5 ± 1
	Reduced #2	-0.52 ± 0.05	4 ± 2	------	------
	Full	-15.0 ± 0.2	-28.22 ± 0.09	0.14 ± 0.05	0.8 ± 0.2
20s	Reduced #1	-1.6 ± 0.1	-7.9 ± 0.8	------	------
	Reduced #2	-0.44 ± 0.05	-0.8 ± 0.4	------	-------

[1] See footnote to table I.

[2] The numbers reported here are for the control volume nearest to the wall, such that the mass flux in the control volume is non-zero. See text for a further explanation of "significant wall mass flux".

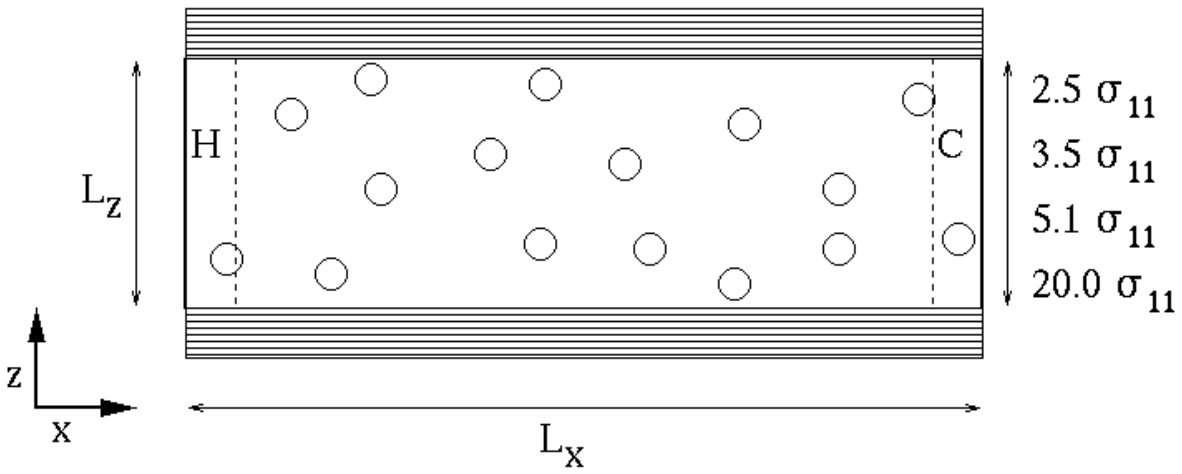
FIGURE CAPTIONS

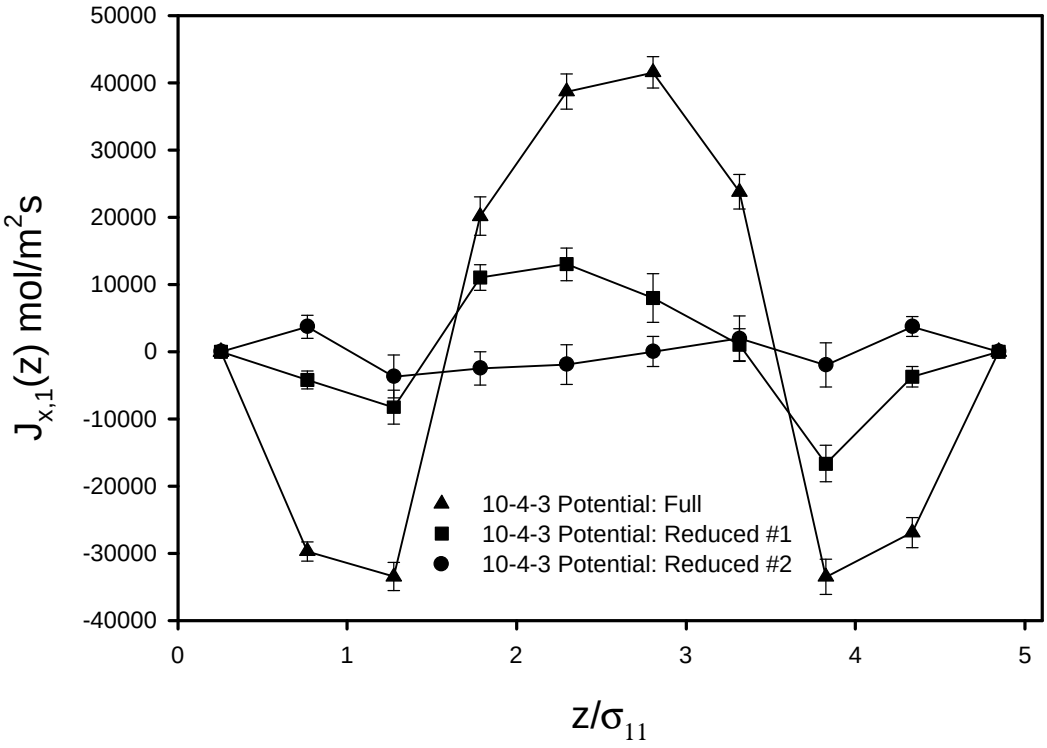
Fig. 1. Layout of the nonequilibrium molecular dynamics simulation cell.

Fig. 2. Mass flux parallel to the wall as a function of wall distance for the 5.1s pore with various attractive potentials.

Fig. 3. Mass flux parallel to the wall as a function of wall distance for the 20s pore with various attractive potentials.

Fig. 4. Two-dimensional (*x*,*z*-projection) flow pattern in the 20s simulation cell.


H
C
L_z
L_x
z
x
2.5 σ_{11}
3.5 σ_{11}
5.1 σ_{11}
20.0 σ_{11}


50000
40000
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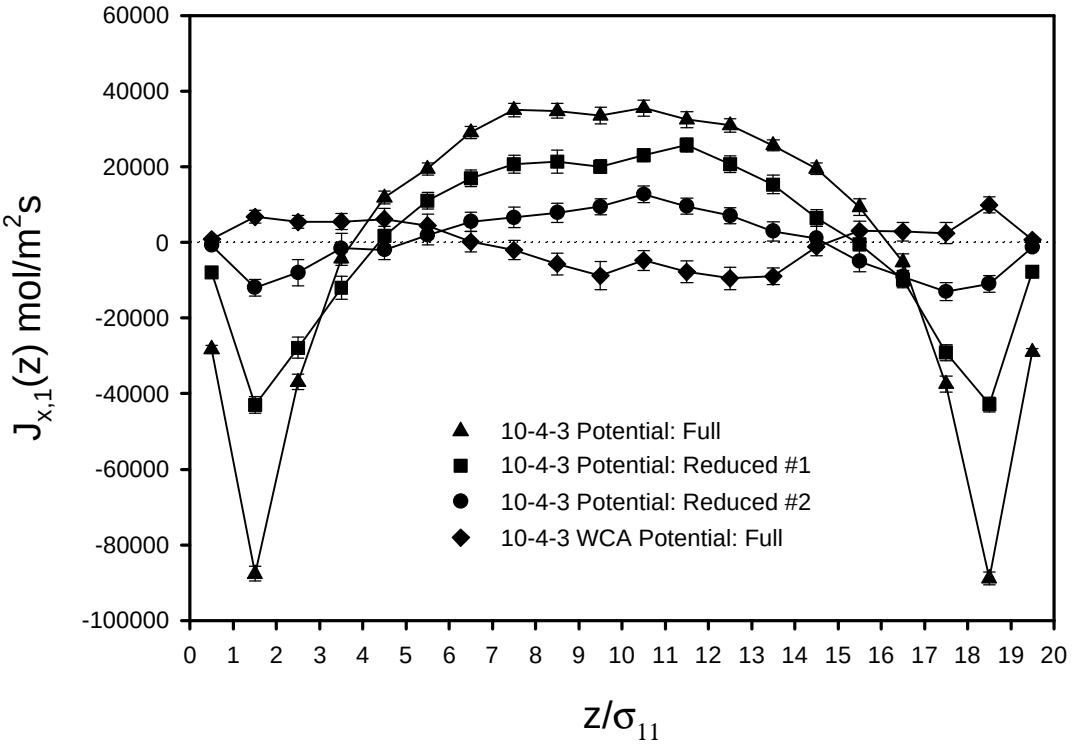
10000
0
-10000
-20000
-30000
-40000
0
1
2
3
4
5
$J_{x,1}(z)$ mol/m^{2}s
z/σ_{11}
10-4-3 Potential: Full
10-4-3 Potential: Reduced #1
10-4-3 Potential: Reduced #2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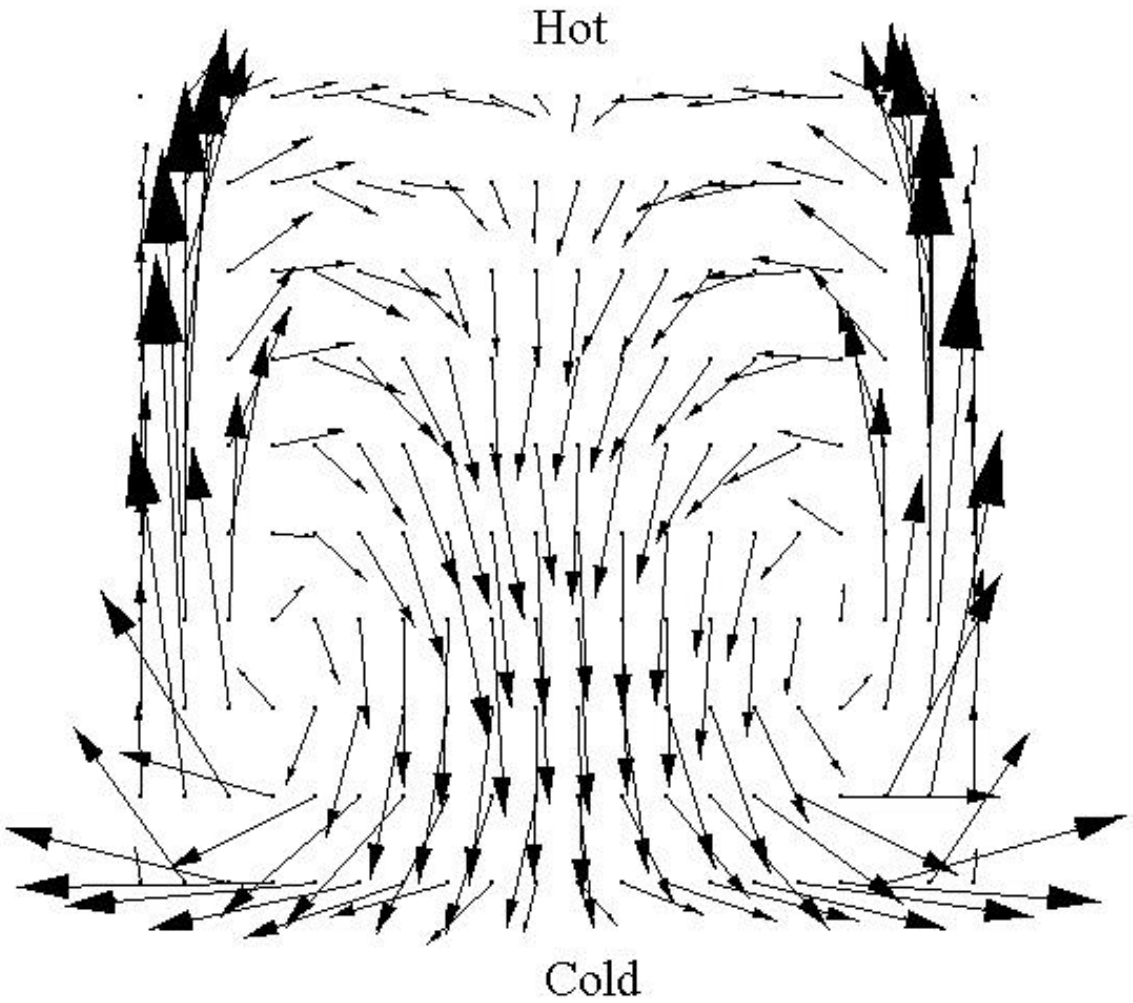
40000
20000
0
-20000
-40000
-60000
-80000
-100000
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20
$J_{x,1}(z)$ mol/m^{2}s
z/σ_{11}
10-4-3 Potential: Full
10-4-3 Potential: Reduced #1
10-4-3 Potential: Reduced #2
10-4-3 WCA Potential: Full


Hot
Cold