Implicit particle wall boundary condition in molecular dynamics

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Abstract: Thin film and nano-tube manufacturing, micro-channel cooling, and many other similar interesting techniques demand the prediction of heat transfer characteristics at the nanometre scale. In this respect, the transport properties at gas–solid and liquid–solid interfaces are very important. The processes at these interfaces can be studied in detail with molecular dynamics (MD) simulations. However, the computational cost involved in simulating the solid wall currently constrains the size of channels, which can be simulated. Therefore, the solid wall is sometimes replaced by boundary conditions, which often compromise on macroscopic quantities, such as density, temperature, pressure, and heat flux. In the current paper, a new particle wall boundary condition is presented, which is in good agreement with existing boundary conditions, but allows for the pressure calculation. This new boundary condition is based on averaging the contributions of an explicit solid wall and is derived using knowledge on common practices in MD algorithms, such as truncation and shifting. Moreover, it allows for different crystal lattices to be included in the new potential. The applicability of the new method is demonstrated by MD simulations of a gas between two parallel plates at different temperatures and densities. Furthermore, these simulations are compared with explicit wall simulations and existing boundary conditions.

Keywords: molecular dynamics, boundary conditions, wall potentials, nanochannels

1 INTRODUCTION

Miniaturizing of electronic components over the past decades has lead to an increase in power consumption used by these components [1]. To maintain good performance of such devices cooling is essential. Unfortunately, current cooling techniques limit the further miniaturization, and, therefore, development of new microscale cooling techniques is essential. Examples of such new techniques are micro and nano-channels, which use a gas or liquid flow to cool the device locally. Consequently, it is important to understand the transport properties, such as heat flux, of gases at the gas–solid interface.

In systems of microsize flow and transport properties can no longer be described sufficiently by a Navier–Stokes continuum approach, since this approach requires the size of the system being not too small and the gas not very dilute [2]. For smaller length scales, it is possible to change to governing equations of the flow model from the Navier–Stokes equations to the Boltzmann equation, which can be solved using for instance the direct simulation Monte Carlo method or through the Burnett equations [3]. However, at sufficiently small length scales the ‘particle behaviour’ becomes essential and, therefore, particle simulation methods are
necessary, such as molecular dynamics (MD) simulations.

MD can be used to investigate the influence of the gas–solid interface in close detail. In statistical mechanics and chemistry MD has long been used \[4, 5\], and more recently it is also applied to biological systems \[6\]. In MD the Newtonian equations of motion dictated by interacting particles are integrated, resulting in their time evolution. For investigation of the gas–solid interface MD is appropriate, since this technique allows the walls to be modelled explicitly, whereas the continuum approach does not hold close to the interface \[2\].

Recently, a MD study investigating the influence of the gas–solid interface interactions on the heat flow in nano-channels has been reported, in which the behaviour of a gas confined between two plates is investigated \[7\].

Although the recent gain in computational power allows for the study of larger channels with MD, microchannels are still too large to be simulated, due to the huge amount of computational cost. Especially the explicit modelling of the solid wall in MD restrains the simulation size. Therefore, the solid wall is sometimes replaced by a boundary condition. Different types of boundary conditions have been suggested over the years, examples include the reflective and thermal wall \[8, 9\]. Whereas the reflective wall reverts the particle when it hits the wall, the thermal wall introduces a stochastic force on a particle when it strikes the wall, giving the particle on re-entrance a new velocity sampled from a Maxwellian-like probability distribution \[10\].

A major drawback to both the reflective and the thermal wall is that they do not carry any information of the underlying configuration of the solid wall. To be able to include such information, the boundary condition has to be derived from the solid’s point of view. In his pioneering work Lennard–Jones derived such relations for several types of crystals \[11–13\]. Subsequently, Hove and Steele used these relations to derive potentials, which describe the interaction between gas molecules and the solid wall \[14, 15\]. Crucial in these derivations are the lattice sums using Fourier series to arrive at the proposed potential. Based on this work, Abraham \[16\] proposed four types of wall potentials: the Lennard–Jones wall as given by Steele \[17\], the Lennard–Jones \((10-4)\) wall, a Boltzmann weighted wall and the reflective wall. Both the Steele and \(10-4\) wall potential have been used extensively over the years. For instance, the Steele potential has been used in studies of the solvation forces of dense fluids \[18–20\], or the dynamics of liquid-filled pores \[21\] and the \(10-4\) potential has been used in work on the solid–fluid interface \[22\], the flow in micropores \[23\], or in work on the velocity auto-correlation function of confined fluids \[24\].

In the current paper, a new type of wall potential boundary condition is presented, which can be used for any type of solid wall crystal structure. Moreover, specific aspects of the MD routine are incorporated into the potential, such as truncation. It is also shown, although the potential does not result in a force parallel to the wall, the potential contributes to the pressure components perpendicular and parallel to the wall. Using this new potential several simulations of a gas confined between two parallel plates at different temperatures and with different bulk densities, ranging from rarefied to dense, are performed. Perpendicular to the walls the density, temperature, heat flux, and pressure profiles have been obtained when the system is in equilibrium. For comparison also MD simulations with explicit solid walls, while keeping the walls at one temperature comparable to the simulations with the new boundary condition are performed. Furthermore, the results are compared with Steele and \(10-4\) boundary condition.

2 MODEL

Many solids have a specific crystal structure, for example a simple cubic (SC), face centred cubic (FCC) or body centred cubic (BCC). In Fig. 1, these three types of crystal structures are schematically depicted. Since both the FCC and BCC lattice can be constructed by combining multiple SC lattices, the derivation of the new potential is performed with the SC lattice. Extending the model to the FCC or BCC case is relatively easy.

The points of one layer in the SC lattice can mathematically be defined in terms of the distance \(\lambda\) between two adjacent lattice points (Fig. 2). In the case of a SC lattice, this distance is similar to the lattice constant \(\kappa\), which gives the shortest distance between any two lattice points. In case of lattices of atoms, this distance is equal to the sum of the Van der Waals radii of two individual atoms.

Assume a gas particle is at a distance \(z\) from the multi-layered SC solid wall (Fig. 2(a)), where the distance \(z\) is measured with respect to the plane going...
through the centres of the atoms in one layer of the crystal lattice. For convenience, set the first layer of the lattice to be at \( z = 0 \). Between the gas particle, located at coordinates \( x, y, \) and \( z \), and any particle of the solid wall the interaction energy can now be calculated. In most MD systems, as well as in this system, the forces arising from the interaction between particles are conservative and central, therefore, it can be written for the potential energy \( \hat{V} \) of the gas particle due to the first layer of the lattice

\[
\hat{V}(x, y, z) = \sum_{i,j \in \mathbb{Z}} V(x - i\lambda, y - j\lambda, z)
\]

where \( V(x - i\lambda, y - j\lambda, z) \) is the potential energy function due to the interaction of the gas particle with one lattice particle located at \( (i, j) \) for any integer value of \( i \) and \( j \). The contribution of the second layer is found by changing \( z \) to \( z + \lambda \) in the expression above, and so on for any other layer.

Instead of the explicit calculation, the objective is to introduce a new boundary condition for the solid wall. Writing equation (1) as an elementary function instead of the double summation seems appropriate. Unfortunately, this can be very laborious, except when some assumptions are made. Replacing equation (1) by the average over \( 0 \leq x < \lambda, 0 \leq y < \lambda \), which is depicted by the shaded area in Fig. 2(b), the average potential energy of a single gas particle due to the interaction with one layer of the solid wall can be written as

\[
U(z) = \frac{1}{\lambda^2} \int_0^{\lambda} dx \int_0^{\lambda} dy \hat{V}(x, y, z)
\]

where it is assumed that the wall particles remain at their lattice points at all time. Inserting equation (1) into the above equation yields

\[
U(z) = \frac{1}{\lambda^2} \sum_{i,j \in \mathbb{Z}} \int_0^{\lambda} dx \int_0^{\lambda} dy V(x - i\lambda, y - j\lambda, z)
\]

It is easily seen that each point \( (x, y) \in \mathbb{R}^2 \) occurs exactly once in each of the integrals in equation (3). Hence, this expression can be rewritten as

\[
U(z) = \frac{1}{\lambda^2} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy V(x, y, z)
\]

The above obtained expression is valid for any central potential.

In most MD systems non-bonded interactions, such as between gas and solid wall particles, are modelled by a Lennard–Jones (LJ) potential

\[
V_{\text{LJ}}(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right]
\]

where \( \varepsilon \) is the characteristic energy in the pair potential, \( \sigma \) the characteristic length of the pair, and \( r \) the scalar distance between the two particles. Since the Lennard–Jones potential decays rapidly to zero for large \( r \), it is often truncated beyond a certain cut-off length, \( R_c \), and shifted in such a way that the potential energy function remains continuous. This results in the truncated shifted Lennard–Jones (TSLJ) potential, which is derived from the standard LJ potential as

\[
V_{\text{TSLJ}}(r) = \begin{cases} 
V_{\text{LJ}}(r) - V_S & \text{if } r \leq R_c \\
0 & \text{if } r > R_c 
\end{cases}
\]

where \( V_S = V_{\text{LJ}}(R_c) \) and is referred to as the shift function [4–6]. The potential function in equation (4) is thus replaced by this TSLJ potential. It is by using this TSLJ potential that the approach differs considerably from previous work [11, 14, 15]. This allows to compute the integral of equation (4) directly, instead via Fourier space, since by using the TSLJ potential the crystal lattice does not extend to infinity. By using polar coordinates, for the average potential energy caused by one layer of the crystal lattice is obtained

\[
U(z) = 2\pi\varepsilon \left( \frac{\sigma}{\lambda} \right)^2 \left[ \frac{2}{5} \left( \frac{\sigma}{\lambda} \right)^2 - \left( \frac{\sigma}{\lambda} \right)^4 \right] \frac{\pi V_S}{\lambda^2 z^2} - 2\pi\varepsilon \left( \frac{\sigma}{\lambda} \right)^2 \left[ \frac{12}{5} \left( \frac{\sigma}{R_c} \right)^2 - 3 \left( \frac{\sigma}{R_c} \right)^4 \right]
\]

which is valid for \( 0 < z \leq R_c \). Furthermore, the second part of the expression is due to the shifting of the truncated LJ potential and the third part by the truncating of the LJ potential. On the other hand, the first part of the expression is identical to the previously mentioned 10−4 potential. Beyond the cut-off distance \( R_c \) the potential equals zero.

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Fig. 2 Side and top view of a gas particle (blue) in close proximity of a SC solid wall (red)
Since the potential energy is pair-wise additive, the total potential energy $U_{SC}$ due to all layers of the SC lattice is given by

$$U_{SC} = \sum_{m} U(z + m\kappa)$$

(8)

where $m$ is the layer number (the first layer has $m = 0$), $\kappa$ the lattice constant, and the prime indicates that only those layers within the cut-off distance $R_c$ have to be taken into account. This last requirement follows immediately from the definition of the TSLJ potential used in equation (7).

The above derivation is valid for a SC lattice, but can easily be extended to the FCC lattice by changing the size of the unit cell and lattice constant. Where for a SC lattice, the lattice constant $\kappa$ and the size of the unit cell $\lambda$ are the same, for a FCC lattice the smallest distance between any two lattice points, is no longer along the axis of the unit cell, but along the diagonal (Fig. 1(b)). Hence, the size of the unit cell is $\lambda = \sqrt{2}\kappa$. Substituting this value into equation (4) would give the integral of the potential for one layer of the FCC lattice. Since the FCC lattice layer is basically a combination of two SC lattice layers, shifted with respect to each other, a multiplication by two is involved, to obtain the correct potential function for the FCC lattice. Thus, the factor in front of the integral of equation (4) turns out to be $1/\kappa^2$, which is the same as for the SC lattice. Adjacent layers in the FCC lattice are separated by a distance $\lambda/2$, which expressed in terms of the lattice constant equals $\kappa/\sqrt{2}$. The total potential energy due to all layers for the FCC lattice is

$$U_{FCC} = \sum_{m=0} U \left( z + \frac{m\kappa}{\sqrt{2}} \right)$$

(9)

where the prime still indicates that the summation is only performed over all layers within the cut-off distance $R_c$.

In Fig. 3, the effective potentials for a SC and FCC lattice are shown, when a cut-off radius of $2.5\sigma$ is employed. Since the FCC lattice has the highest density in the topmost layer, its effective potential has the lowest minimum.

### 2.1 Pressure calculation

The instantaneous pressure for a system of $N$ particles can readily be calculated from the pair interactions in MD [4–6] and is given by the virial equation

$$P = \rho k_B T + \frac{1}{3V} \sum_{i<j} N F_{ij} \cdot r_{ij}$$

(10)

where $\rho$ is the particle density, $T$ the temperature, $V$ the volume, $F_{ij}$ the force exerted on particle $i$ by $j$, and $r_{ij}$ the distance vector between particle $i$ and $j$. The scalar dot product part is known as the virial $W = \sum_{i<j} F_{ij} \cdot r_{ij}$. The first step to derive the pressure contribution is to consider only the contribution to the virial arising from the interaction between a gas particle and the wall. Since the force exerted by the wall on the gas particle is given by the gradient of the wall potential, it can be seen from equation (7) that there is no contribution to the virial by the forces in $x$- and $y$-directions, due to the fact the potential is a function of $z$ only. However, by repeating the method used before to derive the wall potential, it is possible to obtain an expression for the virial that includes the force contributions in the $x$- and $y$-directions. The contribution to the virial that stems from the interaction between a gas particle at position $(x, y, z)$ and all particles in first layer of the wall (at $z = 0$) is given by

$$\hat{W}(x, y, z) = - \sum_{i,j} \frac{\partial V(s)}{\partial s} \cdot s$$

(11)

where $s$ is the vector $(x - i\lambda, y - j\lambda, z)$ and $V$ is the potential that describes the interaction of a gas particle and one wall particle. Similarly to the derivation of the wall potential, the virial $\hat{W}(x, y, z)$ can be approximated for $z > 0$ by the average over
0 \leq x < \lambda, 0 \leq y < \lambda$, giving

\[
W(z) = \frac{1}{\lambda^2} \int_0^\lambda dx \int_0^\lambda dy W(x, y, z) = -\frac{1}{\lambda^2} \int_0^\lambda dx \int_{-\infty}^{\infty} dy \left( \frac{\partial V}{\partial x} x + \frac{\partial V}{\partial y} y + \frac{\partial V}{\partial z} \right)
\]

(12)

The integrals of the first two terms between the brackets, involving only $x$ and $y$, can be rewritten using partial integration, whereas the third term between the brackets can be simplified by taking the derivative with respect to $z$ and multiplication of the integral with $z$ out of the integral. This gives

\[
W(z) = \frac{2}{\lambda^2} \int_{-\infty}^{\infty} dy V(x, y, z) - z \frac{\partial}{\partial z} \frac{1}{\lambda^2} \int_0^\lambda dx \int_{-\infty}^{\infty} dy V(x, y, z)
\]

(13)

Using $U(z)$ as defined in equation (4) allows the approximation of the virial to be written as

\[
W(z) = 2U(z) - z \frac{\partial U(z)}{\partial z} = 2U(z) + zF(z)
\]

(14)

As with the force and the potential energy, the contribution of one gas particle to the virial is a summation of the contributions of all layers within the cut-off distance $R_c$. Hence, again summations like equations (8) and (9) have to be used to obtain the total virial contribution of one gas particle.

3 SIMULATIONS

In order to compare the newly derived boundary condition with the explicit solid wall, MD simulations with the in-house developed program PumMa are performed. The programme is a very efficient parallel MD programme, easily extended to incorporate the new derived boundary condition potential. Recently, PumMa have been used successfully in studies of wall–gas interactions in nano-channels [7, 25], as well as in biological studies of bilayer membrane formation [26], vesicle fusion [27], and fission [28].

3.1 Other wall potentials

Besides comparison with explicitly modelled solid walls, also MD simulations with two other boundary conditions have been performed, which allows comparison to the new potential. Since the new model is derived from the explicit solid wall configuration, comparison seems appropriate with similar types of boundary conditions. Therefore, the new boundary condition potential is compared with the Steele potential [15] and the 10-4 potential [16]. Converted to the units used in the current paper the Steele potential is expressed as

\[
U_s(z) = 2\pi \varepsilon \left( \frac{\sigma}{\lambda} \right)^2 \times \left[ \frac{2}{5} \left( \frac{\sigma}{z} \right)^{10} - \left( \frac{\sigma}{z} \right)^4 - \frac{\sqrt{2}}{3(1+0.61\sqrt{2})} \left( \frac{\sigma}{z} \right)^3 \right]
\]

(15)

and the 10-4 potential, which drops the part with $z^{-3}$, is given by

\[
U_{10-4}(z) = 2\pi \varepsilon \left( \frac{\sigma}{\lambda} \right)^2 \left[ \frac{2}{5} \left( \frac{\sigma}{z} \right)^{10} - \left( \frac{\sigma}{z} \right)^4 \right]
\]

(16)

It should be reminded that these potentials have been derived explicitly for the FCC lattice [16], and, hence, only the value for $\lambda$ belonging to the FCC lattice should be used.

In Fig. 4, both the Steele and the 10-4 potential are shown, together with the new potential, all with the lattice constant belonging to the FCC lattice. From the figure differences between the three potentials are obvious. The Steele and the new potential are very different, whereas the 10-4 potentials follows the new potential for small distances and the Steele potential for larger distances.

The forces due to these potentials are easily calculated. Similar to the new potential only the perpendicular component of the force remains. However, whereas the new potential presented in the current paper allows the explicit calculation of
pressure contributions in the directions parallel to the wall, this is not possible for these two other potentials, since no explicit contributions were given in the original papers. Consequently, only the resulting equation for the force (which is zero for the parallel directions) can be used to determine the pressure contribution. Both the Steele and 10-4 potentials have also been incorporated into the PumMa code.

3.2 Method

Since the interest does not lie with specific gas–wall interactions for either the explicit solid walls, the newly derived potential or the two other potentials, parameters expressed in reduced units are used in the simulations. These units have values typically around one and improve the numerical stability of the simulations. Furthermore, they facilitate error estimation and when one wants to model a specific system, they can easily be converted to SI units. The reduced units in the current paper have as unit for length \( \sigma^* \), as unit for mass \( m^* \), and as unit for energy \( \varepsilon^* \). All other reduced units can be derived out of these choices, such as the units for temperature \( T^* \), density \( \rho^* \), pressure \( P^* \), and time \( \tau^* \).

For each different type of boundary condition, either explicit or a wall potential, a similar system has been used in the simulations, only differing due to the different temperatures \( T \) (0.57\( T^* \), 1.01\( T^* \), and 1.5\( T^* \)) and five different particle densities \( n_0 \) (ranging from 0.01\( \rho^* \) to 0.4\( \rho^* \)). The system size is chosen in such a way that the accessible gas volume of the simulation box is equal for both the explicit and wall potential simulations. For the explicit simulations the box size is approximately \( 47 \times 47 \times 37 \sigma^* \), and for the wall potential simulations approximately \( 47 \times 47 \times 31 \sigma^* \). Small variations in the box size between different simulations depend only on the initial temperature. In all cases, the walls are separated from each other in the \( z \)-direction, and in the \( x \)- and \( y \)-directions periodic boundary conditions are used. In the explicit solid wall case the wall consists of 18 000 particles arranged in a FCC lattice, obtained from a previous crystallization simulation [7]. The total number of gas particles in the simulation box ranges from 660 for the lowest gas density \( (n_g = 0.01) \) to 26 500 for the highest gas density \( (n_g = 0.4) \). In Fig. 5, examples of systems with an explicit wall and with wall potentials are shown.

For the explicit wall simulations gas particles are randomly placed between the two parallel plates, depending on the required density. The same initial configurations have been used for all wall potential simulations, except that the box size in the \( z \)-direction is based upon the location of the centre of the density peak of the first layer of the solid wall, ensuring that no particles are placed too close to the wall initially and that the volumes of the explicit and wall potential simulations are equal.

For the explicit simulations, the solid wall is not restricted in any way, except for the Lennard–Jones interactions between the particles upon forming of the FCC crystal. In principle, the walls can move freely through the simulation box. However, since the mass of the wall is large compared with the mass of one gas particle, a single collision hardly affects the wall. Moreover, collisions occur from both sides at an equal rate, keeping the wall fixed at its initial position. Furthermore the crystal is consolidated by a relatively strong Lennard–Jones interaction parameter, \( \varepsilon_{WW} = 6.0 \varepsilon^* \), which prevents the crystal from melting.

Both the gas and, in the case of the explicit wall simulations, wall particles have unit mass and an equal Van der Waals radius resulting in a collision diameter \( \sigma \) for each interaction of 1\( \sigma^* \). The interaction strengths for gas–gas interactions is set to \( \varepsilon_{GG} = 0.5 \varepsilon^* \) and for gas–wall interactions to \( \varepsilon_{GW} = 1.0 \varepsilon^* \). The fact that the gas particles are in the gas phase and the wall particles in the solid phase is solely controlled by the Lennard–Jones parameter \( \varepsilon \).

Since both the Steele and 10-4 potential are derived explicitly for the FCC case, and the crystal structure of the solid wall is a FCC lattice too, the lattice constant \( \lambda \) in the new wall potential is set to resemble a FCC lattice as well.

For every boundary condition, fifteen simulations are performed, resulting in a total of sixty simulations. Every simulation consists of two parts: an equilibrium phase and a production run, in which macroscopic quantities such as density, temperature, pressure, and heat flux are obtained in the direction perpendicular to the wall. With the explicit wall simulations equilibrium is reached by controlling the temperature of the wall by coupling it to an external heat bath, which in its turn heats up or cools down the gas through collisions of gas particles with the...
wall until equilibrium is reached. To ensure equilibrium in the case of the wall potential simulations, the system is coupled to the external heat bath until equilibrium is reached, followed by the production run part in which no temperature is enforced upon the gas. In other words, the first part of the simulation is in the canonical (constant number of particles, constant temperature, and volume) ensemble, whereas the last part is in the microcanonical (constant energy instead of temperature) ensemble. This simulation protocol ensures that both the explicit simulations and wall potential simulations are in equilibrium and that the temperatures of the gases are equal, allowing comparison between explicit and wall potential simulations. Depending on the gas density, simulations are run for 5 000 000 iterations, using a time step of $0.001 \tau^*$, for the lowest gas densities or for 750 000 iterations for the higher densities to ensure sufficient statistics.

3.3 Results

At the top of Fig. 6, the density profiles, normalized with respect to the bulk density, are shown for the simulations with the explicit solid wall at a temperature of $1.0T^*$, and for all five densities. In this profile, the wall is defined to start at the centre of the first lattice layer. From this figure, it is obvious that the wall influences the nearby particles, since the density deviates from the density found in the bulk, which can be seen towards the right of the figure. It is energetically favourable for a particle to be close to the wall, since more neighbours contribute to a lower potential energy of the particle. Consequently this effect is the strongest for rarefied gases, and for high density gases the wall surface can even be saturated, resulting in the formation of a second peak in the density profile just below $2.0\sigma^*$. Furthermore, if the gas density increases gas particles are pressed against the wall, increasing the local density even further.

Similar profiles are constructed for the system with the wall potential derived in this paper, see the bottom of Fig. 6. Although very much similar to the profiles from the explicit solid wall simulations, differences are evident. The density near the wall is lower with the new wall potential than with the explicit solid wall, and the peaks are much narrower. The main reason for this difference is that with the explicit solid wall the surface is not smooth, since particles oscillate at lattice points, in contrast to the new wall potential, which has no explicit particles and is an average across the surface, which is by definition smooth. Hence, particles can penetrate further in the case of the explicit solid wall than with the new wall potential. This accounts for both the lower density peaks as well as their narrowness.

The effect is even stronger when the Steele potential is used, as can be seen in Fig. 7, for a system with bulk density of $0.1\rho^*$ and temperature $1.0T^*$, showing that the Steele potential resembles the FCC lattice poorly. The density for 10-4 potential is almost identical to the new wall potential, although the latter approximates the explicit solid wall better between $1.0\sigma^*$ and $1.5\sigma^*$, but not around the second peak at $2.0\sigma^*$.

For the lower temperature ($T = 0.5T^*$), crystallization at the wall surface is observed in all cases, whereas for the higher temperature ($T = 1.5T^*$), the density peaks near the wall are much lower, since particles have too much kinetic energy to stick to the wall surface for a while.

As expected for systems in equilibrium, the temperature profiles show that the gas is at the desired temperature. This justifies the used simulation protocol for the wall potentials, by equilibrating the systems in the canonical ensemble first, before switching to the microcanonical ensemble for data collection.
Another important property, especially when cooling is desired, is the net flow of heat in the gas, which is given by the heat current vector $\mathbf{q}$. The heat current vector for a system with $N$ particles and pair potentials only, is given by

$$\mathbf{q} = \frac{d}{dt} \sum_{i=1}^{N} E_i \mathbf{r}_i = \sum_{i=1}^{N} E_i \mathbf{v}_i + \frac{1}{2} \sum_{ij} (F_{ij} \cdot \mathbf{v}_i) \mathbf{r}_{ij}$$  (17)

where $E_i$ is the total (both kinetic and potential) energy of particle $i$, $\mathbf{r}_i$ the position vector of particle $i$, $\mathbf{v}_i$ the velocity vector of particle $i$, and $F_{ij}$ and $F_{ij}$ are the inter-particle separation vector and force vector between particles $i$ and $j$, respectively, [29]. Due to the geometry of the system, the focus is only on the $z$-component of this vector, $q_z$. For a system in equilibrium with both walls at the same temperature the net heat flux has to be zero, which should be the case for the systems under investigation.

For all simulations the net heat flux equals zero, although local deviations, especially close to the wall, occur. However, these deviations are most likely caused by the way data are collected perpendicular to the wall. The value for $q_z$ calculated for particle–particle interactions is assigned to the bins of the particle centres only, but since it depends on the inter-particle separation, its value should actually be distributed along all intermediate bins. Todd et al. have presented a different method for calculating the heat flux distribution, based upon their developed method of planes [30, 31]. However, Todd’s method is not implemented in the PumMa code. Furthermore, although the method used in the PumMa code to determine the heat flux distribution leads to anomalies close to the wall, these anomalies are only induced by the data collection method, and not by the potential used to describe the interaction with the wall. Consequently, in order to compare different wall boundary conditions, the used method in this work is still appropriate, since the same method of data collection is used with the explicit solid wall as well as with the wall potentials.

Since the new derivation allowed for the pressure to be calculated exactly, in contrast to the Steele and 10-4 potential, the profile of the pressure for a gas for all simulations at $1.0T^*$ and $0.1\rho^*$ is shown in Fig. 8. Again, as with the heat flux, due to the way pressure values are assigned to the bins, the peaks close to the wall are anomalies of the data collection method. Based upon similar arguments as for the heat flux they still provide a very good method to compare the different boundary conditions. From the figure, it is apparent that the new potential is more in agreement with the explicit solid wall than the Steele and 10-4 wall potentials. Since it is not possible for these two potentials to compute the pressure contributions parallel to the walls, their profiles lack the dip just above $1.0\sigma^*$. This result shows that incorporating the $x$- and $y$-contributions to the pressure is important to obtain the correct pressure profile.

That the new potential is much closer to the explicit solid is even more stressed when the pressure averages of the total system are compared. For low densities, the explicit solid wall and the new potential give almost identical pressures, whereas the other two wall potentials are not in agreement with the explicit solid wall simulations (Table 1). For higher densities the pressures are much more in the same range for all simulations, which is mainly caused by the high density dependence of the pressure. Again, this shows the importance to account for all pressure contributions, something that is possible with the new potential, but not with the other two wall potentials.

### 4 CONCLUSIONS

A new particle wall boundary condition for MD has been proposed to replace explicit solid walls in MD simulations of channels in order to reduce the computational complexity and allow the investigation of larger channels. The new wall potential is derived from averaging the contributions of one layer of the solid wall, to get a function that only depends on the distance to the wall. By applying the common
practice in MD to truncate and shift potential energy function for pair interactions, the integrals can be computed explicitly, using straightforward calculus. Furthermore, this allowed the exact derivation of the contribution to the pressure in the directions perpendicular and parallel to the wall, something not possible with other existing wall potentials, such as the Steele or 10-4 potential.

Simulations of gases at different temperatures and different densities (varying from rarefied to dense gases) showed that the new potential is in good agreement with the 10-4 potential and to a less extend with the Steele potential. All three wall potentials suffer from the fact that they treat the wall as a smooth surface, resulting in density profiles much too narrow compared with the explicit solid wall simulations. Apparently, averaging the lattice surface is not a very good approximation. Similar effects have been observed by Abraham, and as a solution he proposed the Boltzmann weighted wall, which give results that are significantly better in density profiles compared with explicit wall simulations than the 10-4 potential [16].

Furthermore, the net heat flux equalled zero, as expected, whereas the pressure profiles showed the difference between the three potentials. The lack of the pressure components parallel to the wall is a major drawback for the Steele and 10-4 potential.

The fact that the new particle wall potential presented in this paper is an exact solution for the average behaviour of the explicit solid wall, in contrast to the Steele and 10-4 potentials, which are approximations to the average behaviour of the explicit solid wall, makes the new potential different from to the other two. This is stressed even more by the possibility to calculate the components of the pressure tensor explicitly as well.

Moreover, due to the derivation of the new wall potential and by splitting the contributions of the different lattice layers, different types of crystal lattices can be incorporated into the boundary conditions easily. Even lattices consisting of different types of particles (such as an Na–Cl lattice) are possible.

However, the new wall potential is not perfect, since it does not resemble the explicit solid wall perfectly. A major drawback, holding for any type of wall potential, is the impossibility of the potential to transfer heat to or from the system. When constructing the wall potential, it is assumed that the particles making up the lattice used for the derivation (Fig. 2), are immobile. Consequently, any kinetic components are removed from the model and no heat can be transferred as a result. Currently work is done on an extension of the new particle wall boundary condition in order to allow for both the correct heat transfer and to best approximate of the explicit solid wall.

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REFERENCES


