Cosine law for the atomically rough nanopore: Modeling lattice vibrations with a modified Lowe-Andersen thermostat

Martijn G. Verbeek*
Hoorn, The Netherlands

(Received 25 July 2018; revised manuscript received 2 November 2018; published 18 January 2019; corrected 29 January 2019)

This work proposes a simulation technique that can be used to compute the thermal interaction between a rarefied gas and an atomically rough nanopore. A standard pore geometry, the slit pore, is used to derive the correct version of the cosine law in case the wall consists out of individual atoms. Having the correct cosine law drastically reduces the computational cost of calculating the gas-wall pair interaction in the rarefied gas regime since it is no longer necessary to consider a fully flexible crystal lattice. By considering only a small modification of the Lowe-Andersen thermostat, a well-known simulation technique that uses diffusive gas-heatbath collisions, we show how it can be used to incorporate lattice flexibility even if the wall is modeled as a rigid lattice.

DOI: 10.1103/PhysRevE.99.013309

I. INTRODUCTION

The study of transport within nanopores today is an active research area. Practical materials include carbon nanotubes (ultrafast diffusion) [1] and metal organic framework's (large internal surface that can be used for storage of greenhouse gases) [2]. In nanoconfinement, the physical space becomes highly anisotropic, and it is commonly accepted that transport properties of fluids flowing through a confinement differ from those in the bulk. A key parameter in describing the departure from bulk fluid dynamics is the Knudsen number, Kn, defined as the ratio between between the mean free path λ and the characteristic length scale of the system δ. In the case of a nanopore this length scale becomes very small, and the Knudsen number becomes large even at moderate densities. When the Knudsen number becomes large ($\mathrm{Kn} \geqslant 1$) special attention should be given to the gas-wall scattering kernel. In the highly rarefied gas or Knudsen regime (the regime of interest here) molecular transport can be fully attributed to gas-wall collisions.

A crucial parameter in describing the flow past a surface is the tangential momentum accommodation coefficient (TMAC or f), originally introduced by Maxwell [3]. In Maxwell's model f governs the degree of slip at the surface and represents the fraction of particles that are reflected diffusely, while the remainder $1 - f$ is reflected specularly.

Because experimental observation of the TMAC is difficult in systems having pores in the nanometer length scale, numerical simulations may be a useful tool to study the motion of spherical particles near a wall systematically. Two types of simulations can be used. In molecular dynamics (MD) simulations the wall consists of individual atoms and the gas-wall interaction is determined by the (6–12) Lennard-Jones pair potential [4–6] or hard sphere interaction [7]. For instance, Arya *et al.* were able to relate the TMAC to the Lennard-Jones interaction parameters by considering the impinging and the outgoing velocities inside a plane parallel to the wall [4]. However, in their extended Smoluchowski model it was assumed that lattice vibrations were insignificant and the wall was modeled as a rigid lattice [7]. According to the (hard sphere) rigid lattice assumption proposed by Arya *et al.* the gas particle velocity changed orientation upon a collision with the wall but its magnitude remained the same: gas-wall collisions conserve kinetic energy. So we see that the substrate looses its ability to thermalize the gas with gas-interface collisions. Therefore one often considers an appropriate thermostat (even in MD). For instance, Cao *et al.* simulated walls based on the Einstein theory in which wall atoms vibrate around the fcc lattice sites with an Einstein frequency [8]. The (flexible) crystal is then maintained at constant temperature through a velocity rescaling and the gas by coupling it to a Langevin themostat. Jacobtorweihen *et al.* suggested to model lattice vibrations through the inclusion of a modified Maxwellian Lowe-Andersen (MLA) thermostat, thereby transforming the simulation into a constant temperature (NVT) simulation [9–11].

But with MD there appears to be more procedures to compute f besides the one discussed by Arya *et al.* For instance Spijker *et al.* calculated momentum accommodation coefficients for the well-studied platinum surface with velocity correlation profiles instead [5]. They simulated a flexible lattice where the wall was coupled to a Berendsen thermostat and the gas was kept at constant temperature through gas-wall collisions. More recently, Reinhold *et al.* were able to calculate f for various (realistic) rigid lattice surface models by considering the scattering of single molecules using a slightly modified definition of the TMAC. This modified definition enabled them to study momentum accommodation in three dimensions [12]. Nedea *et al.* were able to compute accommodation coefficients by studying the heat flux between two parallel plates [13,14]. Yet they used a flexible wall to compute the TMAC. So we see from studying MD literature that there appear to be two distinct types of atomistic walls that can be considered when calculating the TMAC: a rigid crystal lattice in which the wall atoms have zero thermal

*gustafverbeek@gmail.com

energy, and a flexible crystal lattice in which the wall atoms do possess thermal energy and the wall essentially acts as a thermostat. The theoretical picture given by Arya's extended Smoluchowski model seems to differ from the "experimental setup" described by Cao and others.

Therefore we consider a second type of simulation where gas-wall collisions are modeled according to Knudsen's cosine law [15,16]. The thermal wall scenario states that whenever a particle has crossed the boundary it is emitted back from the wall with a velocity drawn from a particular distribution at a given wall temperature. In this type of simulation diffusive gas-wall collisions do not conserve kinetic energy and the particle velocity may change in both size and orientation.

However, the goal of this paper is to show that it is also possible to define a cosine law for an atomically rough wall. Therefore we present an algorithm to simulate lattice flexibility at a fraction of the cost of a fully flexible wall simulation while retaining the essential physics of a fully flexible substrate. The method involves only a very small modification to the already existing and well-known MLA thermostat [17,18]. We will derive the collision rules for an arbitrary hard sphere pore geometry, but consider the standard slit pore while doing so. The resulting thermostat enables one to perform constant temperature simulations in the rarefied gas regime even if the wall is modeled as a (hard sphere) rigid lattice. We note that once the inner hard sphere thermal interaction is properly accounted for it is straightforward to add a square well step potential and, for instance, consider adsorption at constant temperature.

II. THEORETICAL BACKGROUND

We consider a rectangular box periodically copied in the x and y directions, but not in the z direction. The box side in the periodic directions has length L. In the z direction the length of the box side equals L_z. The N_w wall atoms are given the label 1 and member i has mass m_1, diameter σ_1, and precollisional velocity $\vec{v}_{i1}$. We can assume the wall particle velocities are Maxwell-Boltzmann distributed at wall temperature T_w. The thickness of the wall equals d_w. The N_g gas particles are labeled 2, and particle j has mass m_2, diameter σ_2, and precollisional velocity $\vec{v}_{j2}$.

In the highly rarefied gas regime the gas particles do not interact with each other but they do interact with the wall. From a computational point of view this gas-wall pair interaction may come at a surprisingly high numerical cost. We note that it is possible to consider two types of atomic crystals. A flexible wall in which the atoms possess thermal energy and oscillate around their equilibrium positions. By coupling the wall atoms to a thermostat at wall temperature T_w we see that it is possible to thermostat the gas with gas-wall collisions such that the temperature of the gas (T) equals the wall temperature. However, quite often the wall is modeled as a rigid crystal in which the wall atoms are frozen and $m_1 \to \infty$ and $\vec{v}_1 \to \vec{0}$. The reason is that straightforward computation of all the pair interactions of a flexible wall comes at a computational cost that scales like N_w^2 and given the high number density of the solid this becomes the bottleneck in the present work. In the case of a rigid lattice one only has to compute $N_w \times N_g$ interactions and for a rarefied gas N_g can be set sufficiently low. For the slit pore geometry the computational cost can be reduced even further by replacing one of the two scattering surfaces with a reflective plane. In the nonperiodic z direction two events can then be identified for any given traveling gas particle. First, at distance $z_2 = L_z$ and $v_{z2} > 0$ a specular collision can occur. In this case the velocity component normal to the reflective plane flips sign and the components parallels remain unaltered. The collision time t_2 is then given by

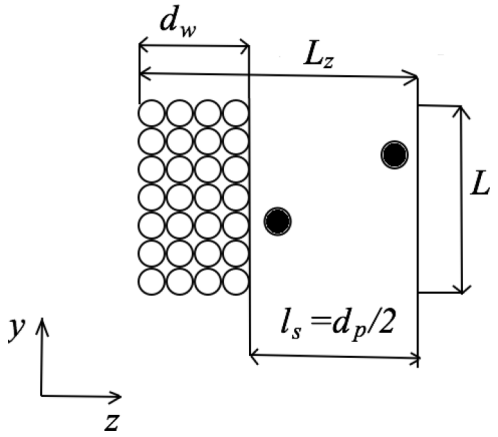

FIG. 1. Cross section of the model slit pore studied here. We consider a wall of a couple of atom layers thick in the z direction, but periodically copied the x and y directions. The box side in the z direction has length L_z. At $z = L_z$ we place a reflective plane of area L^2.

$$t_2 = \frac{L_z - z_2(t)}{v_{z2}}. \tag{1}$$

In general L_z is not equal to L. Furthermore the box size in the z direction (L_z) and the thickness of the wall (d_w) fix the pore diameter (d_p) via $l_s = L_z - d_w = d_p/2$ (see Fig. 1).

When $z_2 \approx d_w$ a hard sphere collision occurs with the atomic scattering surface. The hard sphere collision time is given by

$$t_{12} = \frac{-b_{12} - \sqrt{b_{12}^2 - v_{12}^2\left(r_{12}^2 - \sigma^2\right)}}{v_{12}^2}, \tag{2}$$

where $\vec{v}_{12} = \vec{v}_1 - \vec{v}_2$, $v_{12} = |\vec{v}_{12}|$, $\vec{r}_{12} = \vec{r}_1 - \vec{r}_2$, $r_{12} = |\vec{r}_{12}|$, $b_{12} = \vec{v}_{12} \cdot \vec{r}_{12} < 0$, and $\sigma = \sigma_{12} = (\sigma_1 + \sigma_2)/2$. The smallest of these collision times is chosen to update the positions of the gas particles. In between collisions the gas particles move ballistically and their positions ($\vec{r}_2$) can be updated with

$$\vec{r}_{j,2}(t + \Delta t_k) = \vec{r}_{j,2}(t) + \vec{v}_{j,2}(t)\Delta t_k, \quad \forall j \epsilon [1, N_g]. \tag{3}$$

Here Δt_k is the kth time step and refers to either a 12-pair interaction ($\Delta t_k = t_{12}$) or specular reflection ($\Delta t_k = t_2$). See Ref. [19] for details on the numerical implementation of hard sphere systems.

Suppose $t_{12} < t_2$ and the next collision is one between the gas atom and a wall particle. If we consider a flexible wall

conservation of kinetic energy reads

$$\frac{1}{2}m_1v_1^2+\frac{1}{2}m_2v_2^2=\frac{1}{2}m_1\left(\vec{v}_1+\frac{\Delta p}{m_1}\hat{r}_{12}\right)^2+\frac{1}{2}m_2\left(\vec{v}_2-\frac{\Delta p}{m_2}\hat{r}_{12}\right)^2, \quad (4)$$

where the unit separation vector follows $\hat{r}_{12}=\vec{r}_{12}/r_{12}$. This equation can be solved delivering the momentum change (Δp) for the gas particle, i.e.,

$$\Delta p=-2\mu\vec{v}_{12}\cdot\hat{r}_{12}, \quad (5)$$

with reduced mass $\mu=m_1m_2/(m_1+m_2)$. Therefore the postcollisional velocity of the gas particle $(\vec{w}_2)$ follows

$$\vec{w}_2=\vec{v}_2+\frac{2\mu}{m_2}(\vec{v}_{12}\cdot\hat{r}_{12})\hat{r}_{12}, \quad (6)$$

where $\vec{v}_{12}\cdot\hat{r}_{12}$ is evaluated at the moment of impact, i.e., $r_{12}^2=\sigma^2$. Reconsidering the rigid lattice assumption $m_1\to\infty$ and $\vec{v}_1\to\vec{0}$ then gives

$$\vec{w}_2=\vec{v}_2-2(\vec{v}_2\cdot\hat{r}_{12})\hat{r}_{12}. \quad (7)$$

We see that the gas-wall collision conserves the gas particle kinetic energy since

$$w_2^2=v_2^2, \quad (8)$$

and hard sphere gas-wall collisions can no longer thermostat the gas.

Therefore the goal of this paper is to construct a thermostat in such a way that it is still possible to thermostat the gas with gas-wall collisions, even if we consider the rigid lattice assumption.

We now consider the scheme proposed by Lowe [17,18]. If a thermostat collision occurs the postcollisional velocities $(\vec{w}_1,\vec{w}_2)$ are given by

$$\vec{w}_1=\vec{v}_1-\left(\frac{\mu}{m_1}\right)(\vec{v}_{12}\cdot\hat{r}_{12}-v_{12,n}^{EQ})\hat{r}_{12}$$
$$\vec{w}_2=\vec{v}_2+\left(\frac{\mu}{m_2}\right)(\vec{v}_{12}\cdot\hat{r}_{12}-v_{12,n}^{EQ})\hat{r}_{12}. \quad (9)$$

Here the subscript n is used to highlight that we consider the component of the velocity normal to the scattering surface. In Lowe's original scheme $v_{12,n}^{EQ}$ is sampled from a Maxwellian relative velocity distribution. In the case of a hard sphere physical wall we propose to sample this quantity from the Rayleigh distribtution

$$f^{EQ}(v_{12,n})=\frac{\mu}{k_BT_w}|v_{12,n}|\exp\left(-\frac{\mu v_{12,n}^2}{2k_BT_w}\right), \quad (10)$$

where $v_{12,n}^{EQ}\epsilon[0,\infty)$, k_B is the Boltzmann constant, μ is the reduced mass of the pair, and T_w is the wall temperature. For the rigid lattice assumption $m_1\to\infty$ and $v_{1,n}\to 0$ we obtain

$$f^{EQ}(v_{2,n})=\frac{m_2}{k_BT_w}|v_{2,n}|\exp\left(-\frac{m_2v_{2,n}^2}{2k_BT_w}\right), \quad (11)$$

with $v_{2,n}^{EQ}\epsilon[0,\infty)$ and

$$\lim_{v_{1,n}\to 0}v_{12,n}^{EQ}=v_{2,n}^{EQ}. \quad (12)$$

Celestini *et al.* already noted Eq. (11) is compatible with Knudsen's cosine law [20] and previously we noted that Eq. (11) samples the correct flux of gas particles hitting the wall [16]. Here we wish to demonstrate numerically that Eqs. (11) and (12) represent the correct limit of Eq. (10) when $v_{1,n}\to 0$. Furthermore, and also noted by Lowe, one can define an accommodation probability $P_{\rm acc}$ for a (diffusive) thermostat collision to occur and write

$$\vec{w}_1=\begin{cases}\vec{v}_1-\lim_{m_1\to\infty}2(\mu/m_1)(\vec{v}_{12}\cdot\hat{r}_{12})\hat{r}_{12} & \text{if} \quad \zeta_1>P_{\rm acc}\\ \vec{v}_1-\lim_{m_1\to\infty}(\mu/m_1)\left(\vec{v}_{12}\cdot\hat{r}_{12}-v_{12,n}^{EQ}\right)\hat{r}_{12} & \text{if} \quad \zeta_1\leqslant P_{\rm acc},\end{cases} \quad (13)$$

and

$$\vec{w}_2=\begin{cases}\vec{v}_2+\lim_{m_1\to\infty}2(\mu/m_2)(\vec{v}_{12}\cdot\hat{r}_{12})\hat{r}_{12} & \text{if} \quad \zeta_1>P_{\rm acc}\\ \vec{v}_2+\lim_{m_1\to\infty}(\mu/m_2)\left(\vec{v}_{12}\cdot\hat{r}_{12}-v_{12,n}^{EQ}\right)\hat{r}_{12} & \text{if} \quad \zeta_1\leqslant P_{\rm acc}.\end{cases} \quad (14)$$

Here ζ_1 is uniform random number between zero and one. Note that $\vec{w}_1\to\vec{v}_1$ when $m_1\to\infty$ and assuming the wall particle velocities are Maxwell-Boltzmann distributed we see that $\vec{w}_1\to\vec{0}$, and the wall particle position remains fixed. Written out explicitly we get for the gas particle

$$\vec{w}_2=\begin{cases}\vec{v}_2-2(\vec{v}_2\cdot\hat{r}_{12})\hat{r}_{12} & \text{if} \quad \zeta_1>P_{\rm acc}\\ \vec{v}_2-\left(\vec{v}_2\cdot\hat{r}_{12}+v_{2,n}^{EQ}\right)\hat{r}_{12} & \text{if} \quad \zeta_1\leqslant P_{\rm acc}.\end{cases} \quad (15)$$

The the limit $m_1\to\infty$, where we keep the wall particle positions fixed but update the wall particle velocity with Eqs. (10) and (13) and the gas particle velocity with Eq. (14), the so-called quasirigid lattice (qRL), must be equivalent to the rarefied gas kernel description given by Eqs. (11) and (15) [frozen rigid lattice (fRL)].

A quasirigid lattice computer simulation is organized as follows. We give the wall atoms a large dummy mass $m_1^D\gg m_2$. Each time step we give all the wall particles a small new Maxwellian dummy velocity with components, $v_{\beta 1}^D=\sqrt{k_BT_w/m_1^D}\times\zeta_w$, but keep their positions fixed. Here $\beta=x,y,z$, and ζ_w is a random number drawn from a Gaussian distribution with zero mean and unit variance. Note that $\vec{v}_1^D$ goes to zero when $m_1^D\to\infty$. The wall particle velocity is updated with Eq. (13). Equation (14) is used to update the gas particle velocity. In both cases we have $\vec{v}_{12}=\vec{v}_1^D-\vec{v}_2$ and we sampled $v_{12,n}^{EQ}$ from Eq. (10) with $\mu=m_1^Dm_2/(m_1^D+m_2)$.

For fRL simulations there is no relative velocity since $\vec{v}_{12}=-\vec{v}_2$. Only the gas particle velocities are updated with Eq. (15), and we sample $v_{2,n}^{EQ}$ from Eq. (11). In both

qRL- and fRL simulations gas particle positions are updated with Eq. (3). To see that the Eq. (15) represents the correct limit of Eq. (14) we can compare the corresponding rarefied gas velocity distributions in a particular direction $[g(v_{\beta 2})]$.

We can test if the procedure has been implemented correctly by counting the number of gas-wall collisions $[N_\alpha^{\rm hit}(t)]$ in time, and computing the time average $(\langle N_\alpha^{\rm hit}(t)\rangle)$ and take the time derivative to obtain the collision frequency of interest. For the slit pore geometry with two atomically rough hard sphere walls (where the only relevant collision time is t_{12}) we find

$$\begin{aligned}\nu^\alpha &= \left.\frac{\partial\langle N_\alpha^{\rm hit}(t)\rangle}{\partial t}\right|_{t=0}\\ &= \frac{\langle N_\alpha^{\rm hit}(\Delta t)\rangle - \langle N_\alpha^{\rm hit}(0)\rangle}{\Delta t}\\ &= \frac{\langle N_\alpha^{\rm hit}(\Delta t)\rangle}{\Delta t}\\ &= P_\alpha \frac{\langle N_{\rm total}^{\rm hit}(\Delta t)\rangle}{\Delta t}\\ &= \frac{P_\alpha}{\langle t_{12}\rangle},\end{aligned} \tag{16}$$

where $\langle t_{12}\rangle$ is the average time between two successive gas-wall collisions and α refers to the type of collision that is being considered. Furthermore $P_\alpha = P_{\rm acc}$ for a diffusive collision ($\alpha = $ diff), $P_\alpha = 1 - P_{\rm acc}$ for a hard sphere collision ($\alpha =$ HS), and $P_\alpha = 1$ for the sum of diffusive and hard sphere collisions ($\alpha =$ total). In Eq. (16) we defined P_α as follows:

$$P_\alpha = \frac{\langle N_\alpha^{\rm hit}(t)\rangle}{\langle N_{\rm total}^{\rm hit}(t)\rangle}, \tag{17}$$

and, since $P_{\rm acc}$ is an input constant, note that it should be independent of time. The average collision time $\langle t_{12}\rangle$ can then be defined with

$$\langle t_{12}\rangle = \frac{\Delta t}{\langle N_{\rm total}^{\rm hit}(\Delta t)\rangle}, \tag{18}$$

where Δt is a small time interval during which we count on average $N_{\rm total}^{\rm hit}$ gas-wall collisions. Since t_{12} is accessible during a computer simulation it is straightforward to compute $\langle t_{12}\rangle$ with

$$\langle t_{12}\rangle = \lim_{N_{\rm total}^{\rm hit,run}\to\infty} \frac{\sum_{p=1}^{N_{\rm total}^{\rm hit,run}} \tau_{12,p}}{N_{\rm total}^{\rm hit,run}}. \tag{19}$$

Here we count the total number of gas-wall collisions during a typical simulation run ($N_{\rm total}^{\rm hit,run}$) and do not take the time average. When computing $\langle t_{12}\rangle$ with Eq. (19), the 12-collision interval $\tau_{12,p}$ is given by

$$\tau_{12,p} = t_{c,p} - t_{lc,p}, \tag{20}$$

where $t_{c,p}$ is the current gas-wall collision time, and $t_{lc,p}$ is the last gas-wall collision time. Next the current collision time becomes the last collision time, i.e., $t_{c,p} \to t_{lc,p}$. Having a direct procedure to calculate $\langle t_{12}\rangle$ enables one to verify Eq. (16) numerically. We can now compare the two rigid lattices (qRL and fRL) with each other by comparing the corresponding collision frequencies.

III. NUMERICAL SIMULATIONS

We work with a simulation box that has side of length L in the x and y directions and length L_z in the z direction. Periodic boundaries are applied in the x and y directions but not in the z direction. The pore contains $N_g = 360$ spherical gas particles of diameter $\sigma_1 = 1.0$. The diameter of the gas-wall pair interaction equals $\sigma_{12} = 1.0$. The box side is expressed in units σ the atomic diameter, and its value is $L^* = L/\sigma = 6\sqrt{2}$. For the nonperiodic z direction we have $L_z^* = 5\sqrt{2}$ and we placed a reflective plane at $z^* = L_z$. The wall consists out of 360 particles and the diameter of the wall particles is set equal to $\sigma_1 = 1.0$. The wall is five atom layers thick. Wall particles are organized in a regular fcc lattice [21] with unit cell edge length $a^* = \sqrt{2}$ and $d_w^* \approx 0.5 L_z^*$.

Gas particle positions were updated using Eq. (3) and were given reduced mass $m_2^* = 1.0$. Gas particles do not interact with each other and move ballistically in between gas-wall collisions or reflections. Quantities in this work are reported in reduced units and are marked by an asterisk (*).

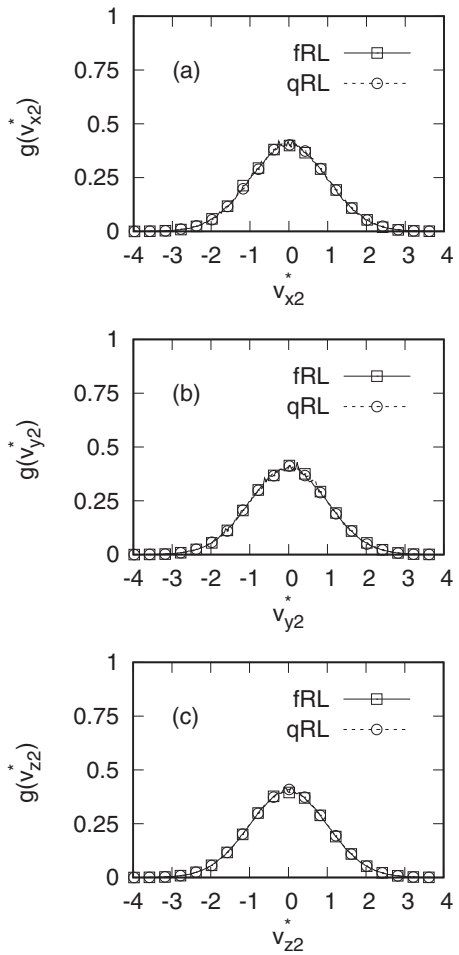

FIG. 2. Plots of the distributions of x, y, and z components of the gas velocity for a qRL (circles) and fRL (squares). Here $P_{\rm acc} = 0.75$.

For the quasirigid lattice (qRL) we set $m_1^{D*} = 1.0 \times 10^{10}$. The wall particles positions were kept fixed but we updated the velocity with Eq. (13) and each time step the wall particles were also given a new Maxwellian distributed dummy velocity ($\vec{v}_1^{D*}$) defined earlier. We also considered the frozen rigid lattice (fRL) where $\vec{v}_{12}^{*} = -\vec{v}_2^{*}$. A first comparison between both lattices is given in Fig. 2. Here we plotted the rarefied gas velocity distributions for the three components x, y, and z. We see an excellent agreement in velocity distribution between both lattices.

Kinetic energy is expressed in units $k_B T$, where k_B is the Boltzmann constant. The reduced wall temperature was fixed to $T_w^* = 1.0$. The reduced gas temperature is designated with T^* and should be equal to T_w^*. This temperature, given in the final column of Table I, can be calculated during a computer simulation.

The reduced unit of the time is $t^* = t/(\sigma\sqrt{m/k_B T})$ and the reduced velocity is $v^* = v\sqrt{m/k_B T}$. The kth time step (Δt_k^*) is given by

$$\Delta t_k^* = \begin{cases} t_2^*, & \text{if} \quad t_2^* < t_{12}^*, \\ t_{12}^*, & \text{if} \quad t_{12}^* < t_2^*. \end{cases} \tag{21}$$

Furthermore we can define an average time step $\langle \Delta t^* \rangle_s$ by sampling Δt_k^* every s time steps, i.e.,

$$\langle \Delta t^* \rangle_s = \frac{1}{n_s} \sum_{l=1}^{n_s} \Delta t_{ls}^*. \tag{22}$$

For instance, a total simulation time of 1.5×10^6 times steps Δt_k^* and sampling interval $s = 50$ would produce $n_s = 3.0 \times 10^4$ sample points for $\langle \Delta t^* \rangle_s$.

The total number of time steps (n_T) was divided into M blocks of length n_B. For sufficiently large n_B we see that $n_T = M \times n_B \to \infty$ and we have the approximation

$$\lim_{n_T \to \infty} \sum_{k=1}^{n_T} \Delta t_k^* \approx \lim_{n_T \to \infty} n_T \langle \Delta t^* \rangle_s, \tag{23}$$

that becomes an equality if we sample every time step ($s = 1$). However, when we counted the gas-wall collisions in time we set $\Delta t_k^* = 1$ so that the block time $t_{1B} = n_B$. We then counted the number of appropriate gas-wall collisions in time per block and took the average over all M blocks. This delivered

TABLE I. $\nu^{\alpha *}$ as a function of accommodation probability P_{acc} for a frozen rigid lattice hard sphere slit pore at reduced wall temperature $T_w^* = 1.0$.

$P_{\text{acc}}(fRL)$	$\nu^{\text{diff}*}$	ν^{HS*}	$\nu^{\text{total}*}$	$\langle t_{12}^* \rangle$	T^*
1.0	47.21	0	47.21	0.0211	1.0
0.8	37.86	9.45	47.31	0.0211	1.0
0.75	35.76	11.94	47.69	0.0211	1.0
0.6	28.43	19.00	47.42	0.0211	1.0
0.4	18.72	28.11	46.83	0.0212	1.0
0.2	9.47	37.82	47.29	0.0211	1.0

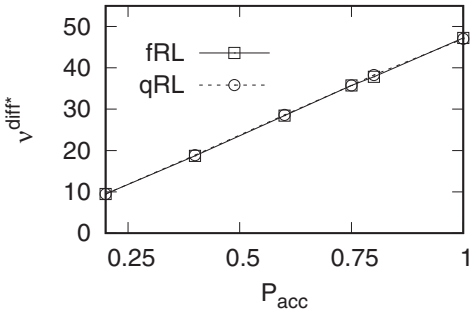

FIG. 3. Plot of the diffusive gas-wall collision frequency as a function of accommodation probability (P_{acc}) for both the quasirigid lattice (qRL) and the frozen rigid lattice (fRL).

the average number of gas-wall collisions in time, i.e.,

$$\left\langle N_\alpha^{\text{hit}}(t_{1n}^*) \right\rangle = \frac{1}{M} \sum_{m=1}^{M} N_\alpha^{\text{hit}}(t_{1m+1n}^*), \tag{24}$$

where M equals the number of time origins and sampling time $t_{1n}^* = n\epsilon[0, n_B)$ and α refers to the type of collision that is being considered (for instance, a diffusive collision). In Eq. (24) we have $t_{1B} = n_B$ and $t_{1m+1n}^* = (m-1) \times t_{1B} + t_{1n}^*$. At the beginning of each block we reset all gas-wall collision frequencies back to zero ($\langle N_\alpha^{\text{hit}}(t_{1m}^*) \rangle = 0$) and start counting all over again. This way of dividing the total simulation time into blocks of a fixed length enables us to compute the time average $\langle N_\alpha(t^*) \rangle$ that can be plotted against the reduced time $t_n^* = n\langle \Delta t^* \rangle_s$ with $n\epsilon[0, n_B)$. In this work we computed the quantity $\langle N_\alpha(t^*) \rangle$ as follows. A typical simulation run contains $M = 100$ blocks and each block has a length $n_B = 1.5 \times 10^4$ time steps Δt_k^*. For an accurate measurement of the velocity distribution we suggest $M \geqslant 200$. We sampled the time step every $s = 100$ time steps delivering $\langle \Delta t^* \rangle_{100} \approx 0.011$. A linear fit of the type $\nu^{\alpha *} t^*$ delivered the gas-wall collision frequency.

Alternatively one can compute $\langle t_{12}^* \rangle$ directly with Eq. (19) without taking a time average (see sixth column of Table I), and compute $\nu^{\alpha *}$ with Eq. (16). Both methods of computation can now be compared. As can be seen from the results in Table I, the agreement is excellent thereby verifying Eq. (16) numerically.

We compared the diffusive gas-wall collision frequency of the frozen rigid lattice ($\vec{v}_{12}^{*} = -\vec{v}_2^{*}$) with the quasirigid lattice [$\vec{v}_{12}^{*} = (\vec{v}_1^{D*} - \vec{v}_2^{*})$] diffusive gas-wall collision frequency. This is shown in Fig. 3. The agreement between the two is excellent, thereby verifying that the method was implemented correctly.

IV. DISCUSSION AND CONCLUSION

We propose a very small modification to the well-known (Maxwellian) Lowe-Andersen thermostat to model the correct thermal gas-solid interactions clearly present in the rarefied gas regime. Like the original MLA thermostat the modified (Rayleigh) Lowe-Andersen thermostat is local, easy to implement, and computationally inexpensive. From a computational point of view such a thermostat drastically speeds up the calculation at the gas-solid interface since it is no

longer necessary to consider a fully flexible crystal lattice. The procedure proposed here enables one to perform constant temperature simulations even if the wall is modeled as a hard sphere rigid lattice.

[1] A. I. Skoulidas, D. M. Ackerman, J. K. Johnson, and D. S. Sholl, Rapid Transport of Gases in Carbon Nanotubes, Phys. Rev. Lett. **89**, 185901 (2002).

[2] P. Canepa, N. Nijem, Yves J. Chabal, and T. Thonhauser, Diffusion of Small Molecules in Metal Organic Framework Materials, Phys. Rev. Lett. **110**, 026102 (2013).

[3] E. H. Kennard, *Kinetic Theory of Gases* (McGraw-Hill, New York, 1938).

[4] G. Arya, H. C. Chang, and E. J. Maginn, Molecular simulations of Knudsen wall-slip: Effect of wall morphology, Mol. Simul. **29**, 697 (2003).

[5] P. Spijker, A. J. Markvoort, S. V. Nedea, and P. A. J. Hilbers, Computation of accommodation coefficients and the use of velocity correlation profiles in molecular dynamics simulations, Phys. Rev. E **81**, 011203 (2010).

[6] W. W. Lim, G. J. Suaning, and D. R. McKenzie, A simulation of gas flow: The dependence of the tangential momentum accommodation coefficient on molecular mass, Phys. Fluids **28**, 097101 (2016).

[7] G. Arya, H.-C. Chang, and E. J. Maginn, Knudsen Diffusivity of a Hard Sphere in a Rough Slit Pore, Phys. Rev. Lett. **91**, 026102 (2003).

[8] B.-Y. Cao, M. Chen, and Z.-Y. Guo, Temperature dependence of the tangential momentum accommodation coefficient for gases, Appl. Phys. Lett. **86**, 091905 (2005).

[9] S. Jakobtorweihen, M. G. Verbeek, C. P. Lowe, F. J. Keil, and B. Smit, Understanding the Loading Dependence of Self-Diffusion in Carbon Nanotubes, Phys. Rev. Lett. **95**, 044501 (2005).

[10] S. Jakobtorweihen, C. P. Lowe, F. J. Keil, and B. Smit, A novel algorithm to model the influence of host lattice flexibility in molecular dynamics simulations: Loading dependence of self-diffusion in carbon nanotubes, J. Chem. Phys. **124**, 154706 (2006).

[11] S. Jakobtorweihen, C. P. Lowe, F. J. Keil, and B. Smit, Diffusion of chain molecules and mixtures in carbon nanotubes: The effect of host lattice flexibility and theory of diffusion in the Knudsen regime, J. Chem. Phys. **127**, 024904 (2007).

[12] J. Reinhold, T. Veltzke, B. Wells, J. Schneider, F. Meierhofer, L. Colombi Ciacchi, A. Chaffee, and J. Thöming, Molecular dynamics simulations on scattering of single Ar, N_2, and CO_2 molecules on realistic surfaces, Computer & Fluids **97**, 31 (2014).

[13] S. V. Nedea, A. A. van Steenhoven, A. J. Markvoort, P. Spijker, and D. Giordano, Gas-surface interactions using accommodation coefficients for a dilute and a dense gas in a micro- or nanochannel: Heat flux predictions using combined molecular dynamics and Monte Carlo techniques, Phys. Rev. E **89**, 053012 (2014).

[14] S. V. Nedea, A. J. Markvoort, A. Steenhoven, and P. A. J. Hilbers, Heat Transfer Predictions for Micro-/Nanochannels at the Atomistic Level Using Combined Molecular Dynamics and Monte Carlo Techniques, J. Heat Transfer **131**, 033104 (2009).

[15] M. Knudsen, *The Kinetic Theory of Gases* (Methuen, London, 1934).

[16] M. G. Verbeek, Smoluchowski thermostat: A realistic introduction of the tangential momentum accommodation coefficient, Phys. Rev. E **81**, 046701 (2010).

[17] C. P. Lowe, An alternative approach to dissipative particle dynamics, Europhys. Lett. **47**, 145 (1999).

[18] E. A. Koopman and C. P. Lowe, Advantages of a Lowe-Andersen thermostat in molecular dynamics simulations, J. Chem. Phys. **124**, 204103 (2006).

[19] M. P. Allen and D. J. Tildesley, *Computer Simulations of Liquids* (Oxford Science Publications, Oxford, 1987).

[20] F. Celestini and F. Mortessagne, The cosine law at the atomic scale: Toward realistic simulations of Knudsen diffusion, Phys. Rev. E **77**, 021202 (2008).

[21] J. M. Haille, *Molecular Dynamics Simulations: Elementary Methods* (John Wiley & Sons, New York, 1992), p. 132.

Correction: The title was not updated properly and has been fixed.