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# Thermal walls in computer simulations

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The physical effects associated with the implementation of two different types of thermal (or stochastic) walls that could be used in computer simulations are considered. The effects of these boundary conditions are first demonstrated using the ideal-gas model and then their influence on interacting particles (with an example of hard spheres) is discussed. [S1063-651X(98)50501-6]

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Idealized molecular models of statistical mechanics—the ideal gas and the hard sphere systems—are valuable as the basis for any more complex and realistic description of existing systems and often as the very foundation upon which other theories are erected. There are strong reasons for first studying the simplest system exhibiting a property of interest—frequently the very essence of a property best reveals itself in the simplest of cases where it occurs, unobscured by the complexities arising in more sophisticated situations. One of the problems pertaining to molecular systems is the effect of (solid) boundaries on a finite size system and microscopic modeling of the boundary conditions. In a classic study [1], Maxwell made the first attempt at expressing ''the conditions which must be satisfied by a gas in contact with a solid wall.'' He considered two types of surfaces for walls: a perfectly smooth surface and a highly uneven, low-density granular surface. Each molecule that strikes the perfectly smooth surface is specularly reflected. Each molecule that strikes the granular surface undergoes a series of collisions within the surface with different surface molecules, and as a result, its ''escape'' velocity becomes randomized and uncorrelated with its initial velocity. The distribution of velocities of the molecules leaving this surface will be determined by the temperature of the wall. We shall call walls of this type thermal walls. Maxwell performed his own calculations under the assumption that a fraction $f$ of a surface is thermalizing and a fraction $1-f$ is reflecting.

With advances in molecular simulations and interest in confined geometries [2–4], the problem of modeling boundaries microscopically is again of central interest. For simulations where the precise microscopic structure of the walls is unimportant, the simplest choices for models for walls are those introduced by Maxwell: the reflective and the thermal walls. The implementation of reflective boundaries is straightforward (the normal component of a molecule impinging on the wall is reversed, the tangential component remains unaltered). The implementation of thermal walls, on the other hand, seems to have been carried out in two different ways in the literature. In order to model a system of particles in thermal contact with a thermal reservoir, one must properly take into account the velocity distribution of particles entering and exiting such a reservoir [5]. A molecule colliding with a thermal wall (parallel to the $y$-$z$ plane) emerges from the wall with the parallel components of its velocity chosen randomly from a Gaussian distribution at a wall temperature $T_w$ [Eq. (2), $i\in\{y,z\}$] and the magnitude of the normal component of the velocity, $v_x$, sampled from the probability density:

$$\phi_1(v_x)=\frac{m}{k_BT_w}|v_x|\exp\left[-\frac{mv_x^2}{2k_BT_w}\right]. \tag{1}$$

$m$ is the mass of a molecule, $k_B$ is the Boltzmann constant, and the sign of $v_x$ must be chosen appropriately according to the wall location [6–9,2].

Some authors [10–12], though, have stated in their papers that the boundary conditions are ones in which the parallel components *and* and the normal component of the velocity of a particle hitting a wall are all sampled from a Gaussian distribution:

$$\phi_2(v_i)=\sqrt{\frac{m}{2\pi k_BT_w}}\exp\left[-\frac{mv_i^2}{2k_BT_w}\right], \tag{2}$$

where $i\in\{x,y,z\}$. It is likely that this choice has its origin in the false expectation that a wall at a particular temperature must emit particles with a Gaussian distribution corresponding to that temperature. The correct boundary conditions must also take into account the velocity-dependent probability with which particles from the system collide with the wall. In other words, one should sample the flux of the particles leaving the wall rather than the density of those in the wall.

In this note we highlight the physical differences between the $\phi_1$ and $\phi_2$ boundary conditions. Spurious physical effects arise with $\phi_2$ and lead to incorrect results in the simulations. Specifically, the case of $\phi_2$ results in (1) an internal temperature [13] that is different from the expected value, (2) possible deviations from the Maxwellian velocity distribution, and (3) inhomogeneities in density and temperature profiles.

To demonstrate the effects of these boundary conditions on molecular systems, let us first consider their influence on an ideal gas. We choose this system for the very reasons described above: the effects of walls are distinct and unconcealed by any other influences (e.g., particle-particle interac-

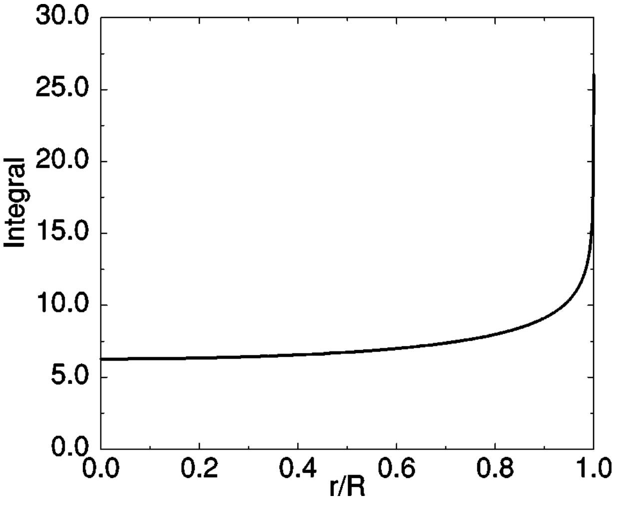

FIG. 1. A plot of the elliptic integral in Eq. (5) as a function of $r/R$. The integral is proportional to the local density of ideal-gas particles bounded by a ''thermal'' ring of radius $R$.

tion and external fields). We will further demonstrate that even when the particles are allowed to interact among themselves, the qualitative effects remain.

We begin with the most trivial case: a one-dimensional ideal gas confined between two thermal walls. The probability density of finding a particle at a location $x$ from the left wall and $x-L$ from the right wall $(0\leqslant x\leqslant L)$ depends on the velocity distribution function $\phi$ as

$$\frac{dN(x)}{dx}=\int P dt\int dv_x\phi(v_x)\delta(x-v_xt)+\int P dt\int dv_x\phi(v_x)\delta(x-L-v_xt), \tag{3}$$

where $t$ denotes time, $N$ the number of particles, $P$ a normalization coefficient related to the wall collision probability, and $\delta(x')$ is the Dirac delta function, imposing a constraint relating the time, velocity, and location of interest. The velocity distribution $g$ at a location $x$ becomes

$$g(v_x,x)=\int P dt\phi(v_x)\delta(x-v_xt)+\int P dt\phi(v_x)\delta(x-L-v_xt). \tag{4}$$

Choosing $\phi_1$ for the ''wall distribution,'' Eqs. (4) and (3) reduce to a Maxwellian velocity distribution and a uniform density distribution inside the ''box.'' Selecting the other distribution, $\phi_2$, the probability density becomes non-normalizable, corresponding to evolution towards a configuration where particles have vanishingly small velocities and remain localized at the walls. The mean kinetic energy of the molecules of the system decreases with time.

Because the one-dimensional case is singular, we now consider a two-dimensional ideal gas bounded by a ring of radius $R$. The distributions that result upon letting the gas equilibrate with the walls are (a) for $\phi_1$, the expected and correct uniform density distribution inside the ring, whereas (b) for $\phi_2$, the density distribution can be expressed as an elliptic integral (see Fig. 1):

$$\frac{dN(r)}{2\pi r dr}=\frac{P'}{2}\sqrt{\frac{m}{2\pi k_BT}}\int_0^{2\pi}\frac{d\theta}{\sqrt{1+(r/R)^2-2(r/R)\cos\theta}}, \tag{5}$$

where $r$ is the radial distance from the center of the circle: $0\leqslant r\leqslant R$ and $P'$ is the wall emission per unit time per unit length of the wall. Also, the internal temperature with $\phi_2$ type boundaries is equal to $T_w/2$. One can study other geometries but inhomogeneities persist.

As a final example of the ideal-gas system, let us consider a system that is infinite in two directions and bounded by two thermal walls in the third. (In computer simulations, this would correspond to having periodic boundary conditions in two directions and walls in the third.) This situation clearly bears a strong resemblance to the one-dimensional case discussed above. Again, if the component of the velocity of the emerging particle perpendicular to the wall is chosen from $\phi_1$, the density between the two walls is uniform. If $\phi_2$ is chosen for the wall distribution, particles increasingly tend to have their perpendicular velocity component approach a vanishingly small value and they eventually remain localized in the vicinity of the walls. The internal temperature is reduced to $\frac{2}{3}T_w$.

Considering more complicated systems and allowing particles to interact with each other can somewhat obscure these effects. Let us illustrate this by comparing the ideal gas to the simplest interacting system—one made up of hard spheres. This system is of particular importance in statistical physics as the simplest system exhibiting both solid and fluid phases and an order-disorder transition between them.

In Fig. 2 below, we compare the number density profiles that result using the two boundary conditions with $\phi_1$ and $\phi_2$. The profiles were obtained with hard-sphere molecular-

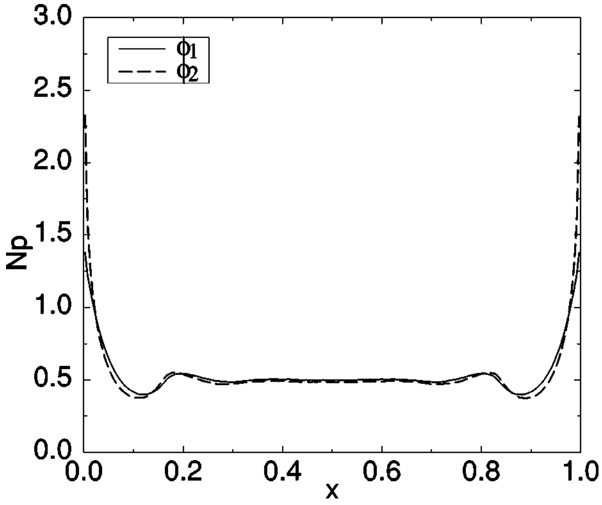

FIG. 2. The number density distribution comparison in the hard-sphere system for the two different thermal walls described in the text. Note the increase in the density at the wallls for $\phi_2$. $Np$ is proportional to number density; $x$ measures the location from the left wall measured in units of the distance between the walls.

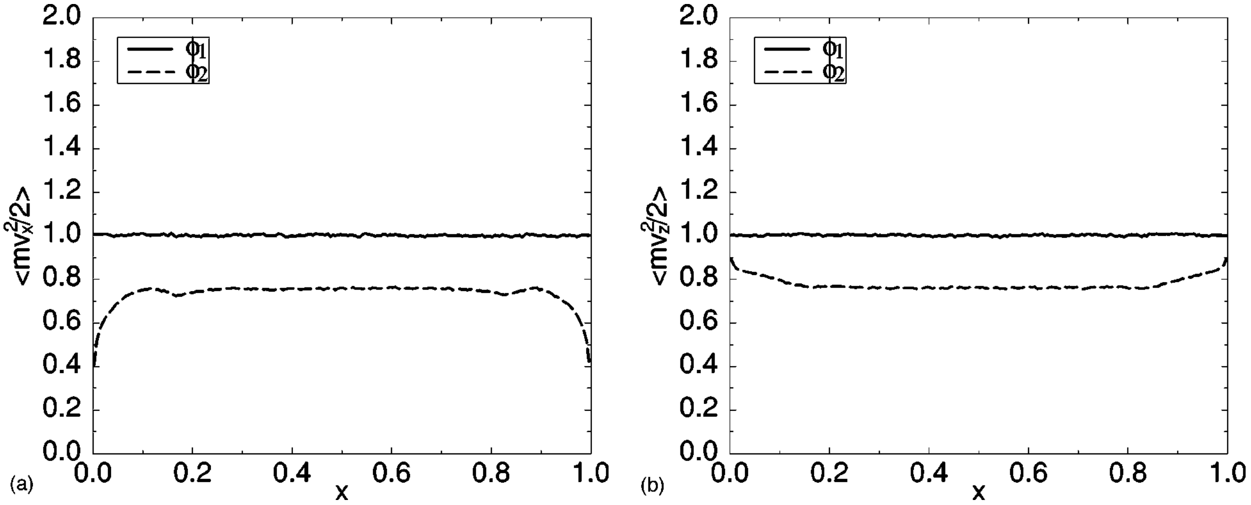

FIG. 3. Profiles of the different contributions to the average kinetic energy per particle in the hard-sphere system for the two different thermal walls described in the text. (a) shows the contribution to the energy from the normal to the wall ($x$) direction $\langle \frac{1}{2} m v_x^2 \rangle$, (b) is the energy contribution from one of the directions parallel to the wall. $\phi_2$ causes inhomogeneities in the average kinetic energy as well as a reduction in its value in the interior of the system. $x$ measures the location from the left wall measured in units of the distance between the walls.

dynamics simulations [14] where Newton's equations of motion are integrated for a system of particles interacting with each other through a hard sphere potential. Hence, all particles move with constant velocities between collisions and their velocities change abruptly during collisions only. The change in velocity in a collision between two particles is determined by momentum and energy conservation. To obtain the number density profiles of Fig. 2, we simulated 108 hard spheres in a three-dimensional box of size $7.1\sigma \times 6.1\sigma \times 6.1\sigma$, where $\sigma$ is the hard-sphere diameter. Periodic boundary conditions were used in the $y$ and $z$ directions while in the $x$ direction studies were carried out with both $\phi_1$ and $\phi_2$ type walls. Starting from an initially uniform distribution of particles, the system was allowed to equilibrate for approximately $2500\tau$ and after the equilibration period, data were collected and averaged over $25000\tau$. The reduced time $\tau$ is defined via the molecular mass $m$, the particle's thermal energy $k_B T$, and the hard-sphere diameter $\sigma$ as $\tau = \sigma\sqrt{m/(k_B T)}$. Contrasting with the ideal gas, hard spheres can collide with each other, and subsequently the state $v_x = 0$ does not have an infinite lifetime and a hard sphere (as opposed to an ideal-gas particle) can escape a wall if another sphere collides with it. Nevertheless, the increase in density near the walls (superimposed on the layering [4]) is strikingly apparent.

In Fig. 3, we show the average kinetic energy (temperature) profiles obtained from the previously described molecular-dynamics simulations with $\phi_1$ and $\phi_2$ boundary conditions. For both distributions, $k_B T_w = 1$. Note the inhomogeneities in the temperature for $\phi_2$ as well as the reduction of the interior temperature.

Thermal walls have been extensively employed in computer simulations for a variety of studies ranging from the modeling of nonequilibrium flows [2], the measurement of velocity and temperature profiles [7], specific heat and the conductivity [11] of fluids in confined geometries, the investigation of non-Newtonian behavior [11], and fluctuations and the onset of convection [12] in fluids, to the breakdown of hydrodynamics [10]. Clearly, a correct realization of thermal walls is necessary to obtain valid results—interesting phenomena could be clouded by an improper application of boundary conditions [15]. In general, the influence of a wall is significant within one mean free path of molecules. Hence employing the correct boundary conditions becomes more crucial for systems whose characteristic size is small compared to the mean free path (the Knudsen number $Kn \gtrsim 1$).

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[13] The internal temperature is defined via the average kinetic energy per particle per degree of freedom $\langle \epsilon \rangle$ as: $T = 2/k_B \langle \epsilon \rangle$.

[14] See, for example, M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Clarendon Press, Oxford, 1987).

[15] After submission of the manuscript, we learned from Michel Mareschal that the correct boundary condition (as described in Ref. [9]) was used in all simulations. The phenomenon studied by Du *et al.* (Ref. [10]) involving the loss of energy of some of the particles is not driven by the boundary conditions at the walls but rather by the inelasticity of the collisions between the particles. Thus their principal results ought to be substantially independent of the choice of boundary conditions. We also learned from Patricio Cordero that even though the velocity distribution on page 490 in the first paper cited in Ref. [11] is the incorrect one, the correct velocity distribution was actually used in the simulations.