HEATING WATER VAPOR IN A SQUARE CAVITY USING MOLECULAR AND PARTICLE MECHANICS

Donald Greenspan

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FAX (817) 272-5802
HEATING WATER VAPOR IN A SQUARE CAVITY USING MOLECULAR
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Donald Greenspan
Mathematics Department
University of Texas at Arlington

Abstract.
This paper explores the computer simulation of heating water vapor in a square cavity. Both molecular and particle mechanics are applied. A particular parameter called \( \text{vel} \), found on the micro level, is shown to be applicable on the macro level in generating both laminar and turbulent flows.

1. Introduction.
Theoretical and experimental studies of the flow of a heated fluid are of broad interest in science and technology. In recent years, related studies have emphasized the Navier-Stokes equations and the continuum point of view. In this paper we will simulate the flow of water vapor in a two dimensional cavity from a discrete point of view, first from the micro, or molecular mechanics point of view, and then from the macro, or particle mechanics point of view. Motion will be induced by heating from below.

We begin by exploring flow on the molecular level. For two water molecules \( P_i \), \( P_j \) which are \( r_{ij} \AA \) apart, an approximate Lennard-Jones potential is [1]

\[
\phi(r_{ij}) = (1.9646)10^{-13} \left[ \left( \frac{2.725}{r_{ij}} \right)^{12} - \left( \frac{2.725}{r_{ij}} \right)^6 \right] \text{erg} \left( \frac{\text{gr cm}^2}{\text{sec}^2} \right).
\]

From (2.1), the force \( \vec{F}_{ij} \) exerted on \( P_i \) by \( P_j \) is

\[
\vec{F}_{ij} = (1.9646)10^{-5} \left[ \frac{12(2.725)^{12}}{r_{ij}^{13}} - \frac{6(2.725)^6}{r_{ij}^7} \right] \frac{r_{ij}}{r_{ij}} \text{dynes} \left( \frac{\text{gr cm}}{\text{sec}^2} \right).
\]

Since the mass \( m \) of a water molecule is \((30.103)10^{-24} \text{ gr} \), equation (2.2) can be simplified to

\[
\vec{a}_i = (160.33)10^{10} \left[ \frac{818.90}{r_{ij}^{13}} - \frac{1}{r_{ij}^7} \right] \frac{r_{ij}}{r_{ij}} \left( \frac{\text{cm}}{\text{sec}^2} \right).
\]

Recasting the latter equation in \( \dot{A}/ps^2 \) (1 sec = \( 10^{12} \) ps, 1 cm = \( 10^6 \AA \)) yields
The effective force on \( P_i \) is not determined by all molecules present, but primarily by those within an interactive distance \( D \), which will be determined by

\[
\frac{dF_{ij}}{dr_{ij}} = 0,
\]

in which \( F_{ij} = ||\vec{F}_{ij}|| \). The solution of this equation yields \( r_{ij} = 3.39 \text{\AA} \). Thus, for \( r_{ij} \geq D = 3.39 \text{\AA} \), we choose \( \vec{F}_{ij} = 0 \). From (2.3), then, the dynamical equation of a molecule \( P_i \) will be for \( r_{ij} < D \)

\[
\ddot{a}_i = (160330.) \sum_j \left[ \frac{818.90}{r_{ij}^3} - \frac{1}{r_{ij}^7} \right] \frac{\vec{r}_{ij}}{r_{ij}} \left( \frac{\text{\AA}}{ps^2} \right).
\]

Next note that \( F_{ij} = 0 \) implies \( r_{ij} = 3.06 \text{\AA} \), so that for \( r_{ij} < 3.06 \) one expects volatile repulsive forces. In addition, for a regular triangle with edge \( 3.06 \text{\AA} \), the altitude is \( 2.65 \text{\AA} \). Using these values we now construct a regular triangular grid of 4235 points in the \( XY \) plane as follows:

\[
\begin{align*}
x(1) &= -91.8, \quad y(1) = 0 \\
x(i) &= x(i-1) + 3.06, \quad y(i) = 0, \quad i = 2, 61 \\
x(62) &= -90.27, \quad y(62) = 2.65 \\
x(i) &= x(i-1) + 3.06, \quad y(i) = 2.65, \quad i = 62, 121 \\
x(i) &= x(i-121), \quad y(i) = y(i-121) + 5.30, \quad i = 122, 4235.
\end{align*}
\]

At each point \((x(i), y(i))\) we set a water molecule \( P_i, i = 1, 4235 \). This array is shown in Figure 1.

To complete the initial data for the molecules, note that at \( 150^\circ C \) and at one atmosphere of pressure, the planar \( rms \) speed \( v \) of a water molecule is [2].

\[
v = (6.23)10^4 \text{ cm/s} = 6.23 \text{ \AA}/ps.
\]

Each molecule is then assigned a speed \( 6.23 \text{ \AA}/ps \) in either the \( X \) or \( Y \) direction, at random, with its sign \((\pm)\) also determined at random.
3. **The Cavity Problem.** The cavity problem to be considered is of the type studied by Rossby [3]. Thus, consider the square basin ABCD, shown in Figure 2, which is 183.6 Å by 183.6 Å. This basin encloses the molecular fluid shown in Figure 1. The four basin sides are called the walls. The problem will be to describe the flow within the cavity when the bottom wall is heated by a linear heating profile.

In each of the examples to be described, simulation was done in double precision on a 64 bit Alpha 275 personal scientific computer. The numerical method used was the leap-frog method [4].

Of computational importance will be a protocol to be applied when a molecule has crossed a wall into the exterior of the cavity. For each of the upper three walls, we will proceed as follows. The position will be reflected back symmetrically, relative to the wall, into the interior of the basin, the velocity component tangent to the wall will be set to zero, and the velocity component perpendicular to the wall will be multiplied by $-1$. If the molecule crosses the bottom wall, then its position $(x, y)$ will be reflected back symmetrically, its $X$ component of velocity will be set to zero, and its $Y$ component of velocity $v_y$ will be determined by the formula

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**Fig. 1** The molecular configuration

**Fig. 2** The closed cavity
\[ v_y = \frac{vel}{183.6} (x + 91.8), \]

in which the parameter \( vel \) is positive. Formula (3.1) is an analogue of Rossby's linear heating profile on the bottom wall, with \( v_y = 0 \) at the leftmost point of the basin bottom and \( v_y = vel \) at the rightmost point. Rossby normalized his formula so as to have temperature 0 at the leftmost point and unity at the rightmost point. Later we will discuss the relationship between the velocity component \( v_y \) at any point and the implied temperature at that point.

A second computational problem derives from the fact that instantaneous velocity fields for molecular motion are Brownian. To interpret gross motion better, we will introduce average velocities as follows. For \( J \) a positive integer, let particle \( P_i \) be at \( (x, (i, k), y(i, k)) \) at \( t_k = k\Delta t \) and at \( (x(i, k - J), y(i, k - J)) \) at \( t_{k-J} = (k - J)\Delta t \). Then the average velocity \( \vec{v}_{i,k,J} \) of \( P_i \) at \( t_k \) is defined by

\[
\vec{v}_{i,k,J} = \left( \frac{x(i,k)-x(i,k-J)}{J\Delta t}, \frac{y(i,k)-y(i,k-J)}{J\Delta t} \right).
\]

In the examples to be described, we will discuss results for various values of \( J \).

4. Examples. Let \( \Delta t = 0.0001 \text{ ps} \) and \( T_k = k(\Delta t), k = 1, 2, 3, \ldots \). For simplicity, the time \( T_k \) will often be denoted by \( T \), when no confusion exists. Thus, for example \( T = 2 = T_{20000} \).

Consider first \( vel = 600 \). Figures 3-6 show the development of a large primary vortex at the respective times \( T = 2, 4, 8, 14 \). In each of these figures the choice of \( J \) was 15000. The actual velocity vectors were reduced by the factor \( mv = 0.31 \) for graphical clarity. Figure 3 shows that on the molecular level, the initial response is that of a compression wave. At its widest, this wave is \( 73 \) \( \AA \) wide, which is consistent with the fact that water vapor is a good conductor of sound. This wave results in compression in the upper left corner of the cavity and volatile molecular repulsion follows, the consequence of which is the onset of rotational motion shown in Figure 4. This rotational motion continues through Figure 5 and culminates in the final primary vortex shown in Figure 6.

Analyses with \( J = 20000, 12000, \) and \( 9000 \) yielded results entirely similar to those described above. For \( vel = 400 \) and \( 800 \) results similar to those for \( 600 \) followed, with the exception that the vortex diameter increased with increasing \( vel \). For \( vel = 50 \) no definitive vortex developed, while for \( vel = 1500 \) the resulting motion showed signs of being chaotic. To explore this latter possibility further, we considered the larger value \( vel = 3000 \), and these results are described next.

For \( vel = 3000 \), the time step had to be reduced to \( \Delta t = 0.00002 \). The input data was that of Figure 6. The flow development is shown in Figures 7-9 at the respective times \( T = 0.3, 0.9, 1.5 \). For graphical clarity, the velocity vectors were reduced by \( mv = 0.04 \). The first indication that the flow in Figure 9 is turbulent comes from the large crosscurrent velocity vectors in the central section of the lower wall, since the onset
of turbulence is marked by a large crosscurrent over the usual direction of vortex flow [5]. Close inspection reveals this to be the case also in the lower left section of Figure 9. Turbulence is then more fully characterized additionally by the rapid appearance and disappearance of many small vortices. By a small vortex we mean the following: For $3 \leq N \leq 6$, a small vortex is defined as a flow in which $N$ molecules nearest to an $(N+1)^{st}$ molecule rotate either clockwise or counterclockwise about this $(N+1)^{st}$ and, in addition, the $(N+1)^{st}$ molecule lies interior to a simple polygon determined by the given $N$ molecules. Figure 10 then shows the 274 small vortices of Figure 9, and further calculation revealed that these disappear quickly while new ones appear.

5. Remarks.

One of the major hopes of researchers using molecular mechanics is that their results in the small will extend to the large (see, e.g., [7]). However, our results do yield great cause for concern for the following reason. The two dimensional formula relating temperature and velocity of a water molecule is [1]

$$T_K = \frac{1}{k} \left( \frac{1}{2} m v^2 \right),$$

in which $T_K$ is the temperature Kelvin, $k$ is the Boltzmann constant $(1.381) \times 10^{-16}$, $m$ is the mass in grams, and $v$ is the speed in cm/s. Thus, for $vel = 600 \, \text{Å/ps}$,

$$T_K = \frac{1}{(1.381) \times 10^{-16}} \left( \frac{1}{2} \left( 30.103 \right) \times 10^{-24} \left( 600 \times 10^4 \right)^2 \right) = 3923635^\circ \text{K}.$$

Thus, on the molecular level, the temperature at the right end point of the bottom basin wall corresponding to $vel = 600 \, \text{Å/ps}$ is approximately $4000000^\circ \text{K}$. Thus, to achieve the vortex motion in Figure 6 requires a temperature far in excess of that required to achieve vortex motion in the large. The reasonableness for this temperature on the molecular level lies in the fact that the motion in Figure 6 results after only 14 ps, that is, after only $14 \left( 10^{-12} \right) \, \text{sec}$. A major problem then is to relate the results in the small to those in the large. To do this we will introduce next particle mechanics, in which molecules will be lump massed into particles, which are then treated in a manner similar to that of molecular mechanics. The primary connection between the micro and macro results will be the parameter $vel$. 

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Fig. 7 T=0.3

Fig. 8 T=0.9

Fig. 9 T=1.5

Fig. 10 274 small vortices in Fig. 9
6. **Particle Arrangement and Equations.** Consider now a 30 cm by 240 cm rectangle and in it construct a regular triangular grid with 8479 grid points, as shown in Figure 11, by the recursion formulas

\[ \begin{align*}
x(1) &= -15.0, \quad y(1) = 0.0 \\
x(i) &= x(i - 1) + 1.0, \quad y(i) = 0.0, \quad i = 2, 31 \\
x(32) &= -14.5, \quad y(32) = 0.866 \\
x(i) &= x(i - 1) + 1.0, \quad y(i) = 0.866, \quad i = 33, 61 \\
x(i) &= x(i - 61), \quad y(i) = y(i - 61) + 1.732, \quad i = 62, 8479.
\end{align*} \]

At each grid point \((x_i, y_i)\), set a participle \(P_i\), that is, an aggregate of molecules. Note that the distance between any two neighbors is unity.

Now we wish the particles to behave somewhat like molecules, but because they will be relatively massive, we do not wish them to display the volatility of molecules. Hence, the force between two particles \(P_i\) and \(P_j\) which are \(R_{ij}\) cm apart will be taken to have magnitude \(F\) given by

\[ F = -A \frac{1}{R_{ij}^3} + B \frac{1}{R_{ij}^4} \text{ (dynes)} \]

Thus,

\[ \phi = -A \frac{1}{2R_{ij}^2} + B \frac{1}{4R_{ij}^4} \text{ (ergs)} \]

Our first problem is then to determine \(A\) and \(B\). Assume that \(F(1) = 0\), so that from (6.1),

\[ -A + B = 0 \]

In order to determine a second equation, some relevant observations must be made first.

Note that the number \(N\) of molecules which can be arranged in the rectangle using the triangular grid approach in Section 2 is

\[ N = \frac{30}{(3.06)10^{-8}} \cdot \frac{240}{(2.65)10^{-8}} = (8.87)10^{18}. \]

Note also that since the mass of a water molecule is \((30.103)10^{-24}\) gr, the total mass \(M\) of the water molecules inside the 30 cm by 240 cm rectangle in Figure 11 is

\[ M = (2.67)10^{-4} \text{ gr}. \]

Distributing this mass over the 8479 particles for conservation of total mass yields an individual particle mass \(m\) of

\[ m = (3.15)10^{-8} \text{ gr}. \]
(6.6) \[ m = (3.15)10^{-8} \text{ gr}. \]

From (2.1) and (6.4), the total potential energy of the molecular configuration, \( E_m \), is approximately

\[
E_m = 3 \sum_{i=1}^{8479} \left\{ (1.9646)10^{-13} \left[ \left( \frac{2.725}{3.06} \right)^{12} - \left( \frac{2.725}{3.06} \right)^6 \right] \right\} = -(1.3)10^6 \text{ erg}.
\]

On the other hand, the total potential energy of the particle configuration, \( E_p \), is from (2.6) approximately

\[
E_p = 3 \sum_{i=1}^{8479} \left[ \left( -\frac{A}{2} + \frac{B}{2} \right) \right] = 25437 \left( -\frac{A}{2} + \frac{B}{4} \right).
\]

Assuming the law of perfect crystals [8], total energy is conserved by setting \( E_m = E_p \), so that, from (6.7) and (6.8), the second equation for \( A \) and \( B \) is

\[
25437 \left( -\frac{A}{2} + \frac{B}{4} \right) = -(1.3)10^6.
\]

The solution of (6.3) and (6.9) is \( A = B = 205 \). Thus, (6.1) takes the particular form

\[
F = 205 \left( -\frac{1}{R_{ij}^3} + \frac{1}{R_{ij}^2} \right).
\]

We assume next that two particles interact only within some local distance of interaction \( D \), which will be determine from \( \frac{dF}{dR_{ij}} = 0 \). Thus, \( D = 1.3 \text{ cm} \).

The dynamical equation of motion of each particle \( P_i \) of the system is given for \( R_{ij} < D \) by

\[
\frac{d^2R_{ij}}{dt^2} = -980 \delta + \alpha \sum_j (205) \left[ -\frac{1}{R_{ij}^3} + \frac{1}{R_{ij}^2} \right] \frac{R_j \vec{R}_{ij}}{R_{ij}},
\]

in which \( \vec{0} = (0, 1) \), \( \alpha \) is a parameter, and \( i = 1, 8479 \). The reason for the introduction of the parameter \( \alpha \) is that the particle interaction forces should be local relative to gravity, that is, gravity must be dominant for \( R_{ij} \) less than, but close to, unity. In the molecular case, the local interaction forces are so large that gravity is relatively insignificant, and hence, did not enter into the equation (2.4). A simple way to achieve this is to set \( \alpha = m \). Then (6.10) reduces to
Fig. 11 A 30 cm by 240 cm rectangular array of particles

Fig. 12 8479 particles

Fig. 7549 particles in a square cavity.
\[ (6.11) \quad \frac{d^2 \vec{R}_i}{dt^2} = -980 \delta + 205 \sum_j \left[ -\frac{1}{R_{ij}^3} + \frac{1}{R_{ij}^5} \right] \frac{\vec{R}_{ij}}{R_{ij}}, \]

and one finds that for \( R_{ij} = 0.9, 0.8, 0.7 \) and 0.6, \( F \) takes the respective values 66, 225, 622, 1687, the first three of which are less than 980.

We now allow the 8479 particles in Figure 11 to find their own equilibrium when interacting in accordance with (6.11). We choose \( \Delta t = 0.0001 \) and use the following reflection protocol. If a particle crosses a wall, it will be reflected back symmetrically, its velocity component tangent to the wall will be set to zero, and its velocity component perpendicular to the wall will be multiplied by \(-1\). The initial motion of the system is almost one of free fall. So, for the first 20000 time steps, each velocity is damped by the factor 0.2 every 2000 time steps. For the next 20000 time steps, each velocity is damped by the factor 0.4 every 2000 time steps. For the third 20000 time steps, the damping factor is 0.7 every 2000 steps. For the final 20000 time steps, the damping is removed. In this fashion, the particles are eased down into the configuration shown in Figure 12. Finally, to obtain a square set of particles, all particles with \( y_i > 30 \) in Figure 12 are removed to yield the 7549 particle set in the square cavity show in Figure 13. It is the positions and velocities of this set which are used as initial data for the examples to be described next.

7. **Examples.** We now proceed to heat the particles in Figure 13. The computational considerations are entirely analogous to those of Section 4 with the notable exception that heat formula (3.1) is now replaced in cgs units by

\[ v_y = vel (x + 15.0) / 30.0. \]

Motivated by the examples in Section 4, consider first \( vel = 600 \). For \( \Delta t = 0.00001 \) and \( J = 20000 \), Figures 14-17 show the development of a primary vortex at the respective times 0.2, 0.4, 0.6, 0.8. For graphical clarity the velocity vectors have been reduced by the factor \( mv = 0.04 \). The particle vortex in Figure 17 is entirely similar to the molecular vortex in Figure 6. In addition, similar results followed using \( J = 15000, 11000, 8000 \).

Next, using the results of Figure 17 as initial data, we set \( vel = 3000 \). The resulting flow is shown at \( T = 0.04, 0.08, 0.12 \) in Figures 18-20, respectively, with \( mv = 0.005 \). Figure 20 reveals the strong cross current in the lower central area which is associated with the onset of turbulence. Figure 21 reveals that Figure 20 has 609 small vortices and further calculations showed that these appear and disappear quickly. Most interestingly, Figure 20 is similar to Figure 9, with the noticeable exception that the area of compression in Figure 20 is larger than that of Figure 9.
8. Remarks. It should be pointed our that there is no proof that the 7549 particles in Figure 13 constitute water vapor. We have shown only that these particles have the characteristics of a fluid in that removal of the right wall results in a flow characteristic of fluids. No further definitive statement can be made because, unlike the molecular case, there is no formula relating temperature and velocity for particles.

Second, it should be noted that the existence of small vortices is, in itself, not sufficient to characterize turbulent flow. These must be accompanied by a cross current which destroys part or all of the vortex motion. Indeed, the vortex motion in Figure 17 has the 614 small vortices shown in Figure 22. It may also be that a different definition of a small vortex might be more appropriate.

Finally, note that the methodology of this paper is applicable to any vapor and any gas whose motion is of interest under a heating procedure.
Fig. 14 T=0.2

Fig. 15 T=0.4

Fig. 16 T=0.6

Fig. 17 T=0.8
Fig. 18 $T=0.04$

Fig. 19 $T=0.08$

Fig. 20 $T=0.12$

Fig. 21 609 small vortices in Fig. 20
Fig. 22. 614 small
vortices in Fig. 17

References.
3. J. Rossby, "Numerical experimentation with a fluid heated non-uniformly from
7. G. J. Dienes and A. Paskin, "Computer modeling of cracks", in *Atomistics of