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PARTICLE SIMULATION OF LARGE
CARBON DIOXIDE BUBBLES IN WATER

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ABSTRACT

A method which can be applied to simulate the motion of fluid drops within fluids is described through a detailed study of a prototype problem, that is, the motion of carbon dioxide bubbles in water. The mathematical formulation uses classical molecular type formulas and results in an n-body problem which is solved numerically. The rise of the bubbles is described, as is the motion of the water near the bubbles. For variety, both H_2O water and D_2O heavy water are considered. Only workstation computer capabilities are required.

1. Introduction Mathematicians, physicists, chemists, meteorologists, and engineers have shown interest in fluid drops ¹⁻¹⁰. Many of the modern studies emphasize the fully nonlinear Navier-Stokes equations and related computer simulations. These studies, however, require special, often rather arbitrary, implementation because surface tension, which is fundamental to the physics of fluid drops, is not inherent in the Navier-Stokes equations. In addition, it is not clear to what extent the Navier-Stokes equations are applicable when the resulting fluid motions are turbulent.

In this paper we will develop a particle or molecular type approach ¹¹ to a two dimensional study of the motion of carbon dioxide bubbles in water. The discussion for this prototype problem will contain all the concepts and methods which are essential for three dimensional studies of the motions of fluid drops within fluids.

2. Particle Fluid Models. Let us begin by considering the most basic fluid in science, that is, water. Unless otherwise specified, the term water molecule will represent either an H_2O molecule or a D_2O molecule. Differentiation between the two will be essential only when the discussion will require the concept of mass.

Given two water molecules P_i and P_j , a simplistic classical molecular potential $\phi(r)$ for the pair is the Rowlinson potential ¹²:

$$(2.1) \quad \phi(r_{ij}) = (2.098)10^{-13} \left[\left(\frac{2.65}{r_{ij}} \right)^{12} - \left(\frac{2.65}{r_{ij}} \right)^6 \right] \text{ erg},$$

in which the distance r_{ij} between P_i and P_j is measured in angstroms. From (2.1) it follows that the force $\vec{F}_i$ on P_i due to P_j is

$$(2.2) \quad \vec{F}_i = (2.098)10^{-5} \left[\frac{12(2.65)^{12}}{r_{ij}^{13}} - \frac{6(2.65)^6}{r_{ij}^7} \right] \frac{\vec{r}_{ji}}{r_{ij}} \text{ dynes.}$$

From (2.2) it follows that $F_i(r_{ij}) = \|\vec{F}_i\|$ is given by

$$(2.3) \quad F_i(r_{ij}) = (2.098)10^{-5} \left[\frac{12(2.65)^{12}}{r_{ij}^{13}} - \frac{6(2.65)^6}{r_{ij}^7} \right],$$

from which it follows that $F_i(\bar{r})=0$ implies

$$(2.4) \quad \bar{r}=2.975 \text{ \AA},$$

which is called the equilibrium distance for the force $\vec{F}$.

Consider now a two dimensional, rectangular basin whose base is 23.8 cm and whose height is 23.713 cm. An XY coordinate system is superimposed on the basin as shown in Figure 2.1. The basin is symmetrical about the Y axis and lies in the upper half plane. On the basin we now construct a regular, triangular grid, as shown in Figure 2.2. The triangular building block for the grid has edge 1.19 cm and altitude 1.031 cm, as shown in Figure 2.3. The grid has 24 rows and 492 grid points, which are numbered 1-492 in the usual fashion, left to right on each row and bottom to top.

At each of the constructed grid points, we wish to place a water particle, that is, an aggregate of water molecules. If a point has been numbered i , then the associated particle is denoted by P_i . The mass of each P_i will be determined by distributing equally over the particles the total mass of all the molecules in the basin. Use of (2.4) as the edge of a regular, triangular grid of water molecules implies that the number N of water molecules in the basin is

$$(2.5) \quad N = \frac{(23.8)(23.713)}{(2.975)10^{-8}(2.576)10^{-8}} = (7.364)10^{17}.$$

Now, the mass of a single H_2O molecule is $(30.103)10^{-24}$ gr, so that the total H_2O molecular mass is $(2.217)10^{-5}$ gr. Distributing this over the 492 particles implies that the mass M_1 of an H_2O particle is

$$(2.6a) \quad M_1 = (4.506)10^{-8} \text{ gr.}$$

In a similar fashion, since the mass of a D_2O molecule is twice that of an H_2O molecule, the mass M_2 of a D_2O particle is

$$(2.6b) \quad M_2 = (9.011)10^{-8} \text{ gr.}$$

Fig. 2.1
RECTANGULAR BASIN

Figure 2.3 REGULAR TRIANGULAR
BUILDING BLOCK

Fig. 2.3

Figure 2.2 TRIANGULAR BASIN GRID

Next we wish to develop a formula for the force between two particles P_i and P_j . We assume that the force has a magnitude

$$(2.7) \quad F = \frac{G}{R_{ij}} + \frac{H}{R_{ij}^3} \text{ dynes,}$$

in which the distance R_{ij} between P_i and P_j is measured in cm. From (2.7), then,

$$(2.8) \quad \phi(R_{ij}) = -G \log R_{ij} + \frac{H}{2R_{ij}^2}.$$

Assuming that the basic edge length 1.19 cm of the triangular grid in Figure 2.2 is the equilibrium distance for the force F in (2.7) implies

$$(2.9) \quad \frac{G}{1.19} + \frac{H}{(1.19)^3} = 0.$$

A second equation for G and H is determined by computing potential energies of the particle and molecular systems as follows. Assuming that all velocities are zero, the potential energy E of the particle system is, approximately,¹¹

$$(2.10) \quad E = 3 \sum_{i=1}^{492} \left(-G \log 1.19 + \frac{H}{2(1.19)^2} \right),$$

or,

$$(2.11) \quad E = 3 (492) (-0.17395 G + 0.35308 H),$$

while that for the molecular system is, approximately,

$$(2.12) \quad E = 3 \sum_{i=1}^{(7.364)10^{17}} \left\{ (2.098)10^{-13} \left[\left(\frac{2.65}{2.975} \right)^{12} - \left(\frac{2.65}{2.975} \right)^6 \right] \right\},$$

so that

$$(2.13) \quad E = - (1.159)10^5 \text{ erg.}$$

Thus, (2.11) and (2.13) imply

$$(2.14) \quad -0.4927G + H = -222.4.$$

Finally, the solution of (2.9) and (2.14) is

$$(2.15) \quad G = 116.51, H = -164.99,$$

so that (2.7) becomes

$$(2.16) \quad F = \frac{116.51}{R_{ij}} - \frac{164.99}{R_{ij}^3}.$$

Next, let us develop dynamical equations for H_2O and D_2O particles. Consider first a D_2O particle. From (2.6b) and (2.16), let the motion of P_i be determined by the dynamical equation

$$(2.17) \quad (9.011)10^{-8} \frac{d^2 \vec{R}_i}{dt^2} = -980(9.011)10^{-8} \vec{\delta} + \alpha \sum_{\substack{j=1 \\ j \neq i}}^{492} \left[\frac{116.51}{R_{ij}} - \frac{164.99}{R_{ij}^3} \right] \frac{\vec{R}_{ji}}{R_{ij}},$$

in which $\vec{\delta}=(0,1)$ and α is a normalization constant which is determined as follows. From (2.17)

$$(2.18) \quad \frac{d^2 \vec{R}_i}{dt^2} = -980 \vec{\delta} + \alpha \sum_{\substack{j=1 \\ j \neq i}}^{492} \left[\frac{12.930}{R_{ij}} - \frac{18.310}{R_{ij}^3} \right] 10^8 \frac{\vec{R}_{ji}}{R_{ij}}$$

The normalization constant α is now chosen so that each particle P_i in the very top row of the configuration shown in Figure 2.2 is supported completely by the local interaction with any particle which lies 1.0305 units directly below it (see Figure 2.3). Thus,

$$(2.19) \quad \alpha \left[\frac{12.930}{1.0305} - \frac{18.310}{1.0305^3} \right] 10^8 = 980,$$

from which one finds

$$(2.20) \quad \alpha = (-234.19)10^{-8}.$$

Hence, (2.18) reduces to

$$(2.21) \quad \frac{d^2 \vec{R}_i}{dt^2} = -980 \vec{\delta} + \sum_{\substack{j=1 \\ j \neq i}}^{492} \left[-\frac{3028}{R_{ij}} + \frac{4288}{R_{ij}^3} \right] \frac{\vec{R}_{ji}}{R_{ij}} .$$

For actual computation, we will make the convenient change of variables

$$(2.22) \quad T = 10t ,$$

so that (2.20) becomes finally

$$(2.23a) \quad \frac{d^2 \vec{R}_i}{dT^2} = -9.8 \vec{\delta} + \sum_{\substack{j=1 \\ j \neq i}}^{492} \left[-\frac{30.28}{R_{ij}} + \frac{42.88}{R_{ij}^3} \right] \frac{\vec{R}_{ji}}{R_{ij}} .$$

Observe immediately that since the mass of H_2O is half that of D_2O , the dynamical equation for an H_2O particle is from (2.23a)

$$(2.23b) \quad \frac{d^2 \vec{R}_i}{dT^2} = -9.8 \vec{\delta} + \sum_{\substack{j=1 \\ j \neq i}}^{492} \left[-\frac{60.56}{R_{ij}} + \frac{85.76}{R_{ij}^3} \right] \frac{\vec{R}_{ji}}{R_{ij}} .$$

3. Basin Stabilization. We next let a basin of H_2O particles find its own equilibrium configuration dynamically as follows. Consider then a basin of H_2O particles at the grid points of the triangular grid shown in Figure 2.2. To avoid symmetry, a velocity of either ± 0.0000001 is assigned in the X direction , at random, to each particle. From these initial data, the motion of the system is generated as follows. The dynamical equation of each P_i is taken to be

$$(3.1) \quad \frac{d^2 \vec{R}_i}{dT^2} = -9.8 \vec{\delta} + \sum_{\substack{j=1 \\ j \neq i}}^{492} \left[-\frac{A}{R_{ij}} + \frac{B}{R_{ij}^3} \right] \frac{\vec{R}_{ji}}{R_{ij}} ,$$

in which $R_{ij} > 1.2$ implies $A=B=0$, while $R_{ij} \leq 1.2$ implies $A=60.56$, $B=85.76$. In this fashion, interparticle force is kept strictly local. The resulting 492-body problem is solved numerically by the leap-frog formulas ¹³ with $\Delta T = 0.0002$ on a Silicon Graphics workstation. Every 500 time steps, each velocity is damped by the factor 0.1. Particle reflection due to wall collision is done symmetrically with velocity damped by the factor 0.1. In the usual notation $T_k = k\Delta T, k=0,1,2,\dots$, the evolution of the basin through

Figure 3.1 H_2O BASIN AT T_{20000}

Figure 3.2 H_2O BASIN AT T_{80000}

Figure 3.3 H_2O BASIN AT T_{140000}

Figure 3.4 D_2O BASIN AT T_{140000}

T_{140000} is shown in Figures 3.1-3.3. With the same considerations, the stabilized D_2O basin at T_{140000} is shown in Figure 3.4. At T_{140000} , the maximum value of y for the H_2O basin is approximately 14.4, while that for the D_2O basin is approximately 12.2.

Calculations were halted at T_{140000} because we desired to have a fluid with nontrivial internal and surface motions.

4. Motion of CO_2 Bubbles. To simulate the motion of CO_2 bubbles in H_2O and in D_2O , we must first repeat for a CO_2 gas the considerations in Section 2. Since CO_2 gas in three dimensions at 0° C has a density approximately ¹⁴ 1/500 that of H_2O , in two dimensions the density will be approximately $500^{-2/3}$, or, approximately 1/63 that of H_2O . Thus, into the basin shown in Figure 2.1 we place $(1.169)10^{16}$ molecules and $492/63$, or for convenience, 7 CO_2 particles. The particles are arranged as shown in Figure 4.1.

For the molecular arrangement, note that a potential for CO_2 is ¹²

$$(4.1) \quad \phi(r_{ij}) = (1.132051)10^{-13} \left[\left(\frac{4.07}{r_{ij}} \right)^{12} - \frac{4.07^6}{r_{ij}^6} \right],$$

so that

$$(4.2) \quad F(r_{ij}) = (1.132051)10^{-5} \left[\frac{12(4.07)^{12}}{r_{ij}^{13}} - \frac{6(4.07)^6}{r_{ij}^7} \right],$$

which yields an equilibrium distance of $4.57 \text{ \AA}$. One then has an approximate total molecular potential energy of

$$(4.3) \quad E = 3 \sum_1^{(1.17)10^{16}} \left\{ (1.132051)10^{-13} \left[\left(\frac{4.07}{4.57} \right)^{12} - \left(\frac{4.07}{4.57} \right)^6 \right] \right\}$$

or,

$$(4.4) \quad E = - 993.4 \text{ erg.}$$

For CO_2 particles, we assume

$$(4.5) \quad F = \frac{A}{R_{ij}} + \frac{B}{R_{ij}^3},$$

with R_{ij} measured in cm. Then,

$$(4.6) \quad \phi = -A \log R_{ij} + \frac{B}{2R_{ij}^2}.$$

Assuming that $R=11.9$ cm is the CO_2 particle equilibrium distance implies

$$(4.7) \quad \frac{A}{11.9} + \frac{B}{11.9^3} = 0.$$

The total potential energy of the particle system is, approximately,

$$(4.8) \quad E = 12 \left(-A \log 11.9 + \frac{B}{2(11.9)^2} \right),$$

so that

$$(4.9) \quad 12(-A \log 11.9 + \frac{B}{2(11.9)^2}) = -993.4.$$

The solution of (4.7) and (4.9) is $A=27.800$, $B=-3936.9$.

Finally, since the mass of a CO_2 molecule is $(7.3585)10^{-23}$ gr, the total molecular mass M is

$$(4.10) \quad M = (7.3585)10^{-23}(1.169)10^{16} = (8.602)10^{-7} \text{ gr}$$

and the mass M_3 of a CO_2 particle is

$$(4.11) \quad M_3 = M/7 = (1.2289)10^{-7} \text{ gr}.$$

Thus, the equation of a CO_2 particle is

$$(4.12) \quad M_3 \frac{d^2 \vec{R}_i}{dt^2} = -980 \vec{\delta} M_3 + \alpha \sum \left[\frac{27.800}{R_{ij}} - \frac{3936.9}{R_{ij}^3} \right] \frac{\vec{R}_{ji}}{R_{ij}}.$$

From (2.20) and (4.11), then,

$$(4.13) \quad \frac{d^2 \vec{R}_i}{dt^2} = -980 \vec{\delta} + \frac{(-234.2)10^{-8}}{(1.2289)10^{-7}} \sum \left[\frac{27.800}{R_{ij}} - \frac{3936.9}{R_{ij}^3} \right] \frac{\vec{R}_{ji}}{R_{ij}}$$

or,

$$(4.14) \quad \frac{d^2 \vec{R}_i}{dt^2} = -980 \vec{\delta} + \sum \left[-\frac{529.78}{R_{ij}} + \frac{75025.}{R_{ij}^3} \right] \frac{\vec{R}_{ji}}{R_{ij}} .$$

Hence, by (2.22), we find

$$(4.15) \quad \frac{d^2 \vec{R}_i}{dT^2} = -9.8 \vec{\delta} + \sum \left[-\frac{5.298}{R_{ij}} + \frac{750.25}{R_{ij}^3} \right] \frac{\vec{R}_{ji}}{R_{ij}} .$$

We need next equations of motion for CO_2-H_2O interaction. For H_2O-H_2O and CO_2-CO_2 particle interactions, the equations are (2.23a) and (4.15), respectively. For CO_2-H_2O particle interaction we will use a simple law of empirical bonding¹² in which the local interaction constants are averaged. However, we will also impose a local interaction distance D to force local interaction only. Our choice is $D=1.2$. thus the following dynamical approach will be used. Let P_i and P_j be any two particles in the basin shown in Figure 3.3. The motion of P_i is determined by the dynamical equation

$$(4.16) \quad \frac{d^2 \vec{R}_i}{dT^2} = -9.8 \vec{\delta} + \sum_{\substack{j=1 \\ j \neq i}}^{492} \left[-\frac{A}{R_{ij}} + \frac{B}{R_{ij}^3} \right] \frac{\vec{R}_{ji}}{R_{ij}} .$$

If $R_{ij} > 1.2$, then $A=B=0$. If $R_{ij} \leq 1.2$, then A and B are determined as follows. If P_i, P_j are both H_2O particles, then $A=60.56$, $B=85.76$. If P_i, P_j are both CO_2 particles, then $A=5.30$, $B=750.25$. In all other cases, $A=32.93=0.5(60.56 + 5.30)$, $B=418.01=0.5(85.76 + 750.25)$.

As a first example, consider the H_2O basin shown in Figure 3.3. The particles P_{108} , P_{158} , P_{213} , P_{263} , P_{294} , P_{298} and P_{362} are now assumed to be CO_2 particles. No changes in positions or velocities are made. The initial configuration is shown in Figure 4.2. The system (4.16) was solved numerically with $\Delta T=0.0002$ by the leapfrog formulas through T_{640000} . The natural, rapid bubble emergence from the basin is shown in Figures 4.3-4.8 at the indicated times.

As a second example, the first example was repeated in each detail with the single exception that the basin used was the D_2O basin shown in Figure 3.4. The initial configuration is shown in Figure 4.9. The emergence of the bubbles from the basin is shown typically in Figures 4.10-4.12, at the indicated times. The emergence was, approximately, 0.7 times faster than from the H_2O basin.

Consider finally setting the seven CO_2 particles in the H_2O basin in the positions P_{216} , P_{217} , P_{236} , P_{237} , P_{238} , P_{257} , P_{258} , as shown in Figure 4.13. The effect is to have created a large compressed gas bubble. One must now expect the generation of a compressive wave. With $\Delta T = 0.00002$, the resulting motion is shown in Figures 4.14 - 4.18 at the indicated times. Figure 4.14 shows the immediate compression wave effect directly above the bubble at the basin surface. The figures also show the disintegration of the bubble as it rises. Figure 4.19 shows at T_{160000} only those H_2O particles which were originally below the bubble and their formation into a wake below the CO_2 as it rises. Figure 4.20 shows at this same time how the particles originally at the top of the basin have moved downward toward the area vacated by particles in the wake. A large rotational H_2O motion is evident at this time.

5. Remarks. Models with fewer than 500 particles can be studied easily using most available workstations. Models with many more particles, say, 5000, can yield more accurate information and more esthetic pictures¹¹, but require at present some form of supercomputation. The development of more powerful workstations or of parallel computers will eliminate this requisite.

With regard to the results in Section 4, note that all gross motions were the results of Brownian type motions. Thus, the upward CO_2 motions were the result of both upward and downward oscillations, with the upward ones dominating.

Since we have not defined turbulence, it is unreasonable to claim that portions of the basin motions were turbulent. A possible approach to such flows¹³ would require the use of average velocity vectors and extensive graphs of the resulting velocity fields. This would require more sophisticated techniques than those employed in the present paper.

Figure 4.1 CO_2 PARTICLES

Figure 4.2 INITIAL CO_2 - H_2O CONFIGURATION

Figure 4.4
T=140000

Figure 4.3
T=120000

Figure 4.5 $T=T_{80000}$

Figure 4.6 $T=T_{120000}$

Figure 4.7 $T=T_{180000}$

Figure 4.8 $T=T_{240000}$

Figure 4.9 INITIAL $\text{CO}_2\text{-D}_2\text{O}$ CONFIGURATION

Figure 4.10 $T=T_{20000}$

Figure 4.11 $T=T_{40000}$

Figure 4.12 $T=T_{80000}$

Figure 4.13 INITIAL $\text{CO}_2\text{-H}_2\text{O}$ CONFIGURATION

Figure 4.14 $T=T_{20000}$

Figure 4.15 $T=T_{60000}$

Figure 4.16 $T=T_{160000}$

Figure 4.17 $T=T_{240000}$

Figure 4.18 $T=T_{340000}$

Figure 4.19 WAKE FLOW AT T_{160000}

Figure 4.20 VERTICAL FLOW OF UPPERMOST PARTICLES
AT $T=T_{160000}$

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