INTERNATIONAL JOURNAL FOR NUMERICAL METHODS IN FLUIDS, VOL. 10, 247–257 (1990)

QUASIMOLECULAR SIMULATION OF LARGE LIQUID DROPS

DONALD GREENSPAN

Department of Mathematics, University of Texas at Arlington, P.O. Box 19408, Arlington, Texas 76019, U.S.A.

SUMMARY

Large liquid drops are simulated by molecular aggregates called quasimolecules. The quasimolecules interact in accordance with classical molecular-type formulae. Supercomputer examples are described and discussed for both stationary and falling water drops.

KEY WORDS Water Drop Tension

1. INTRODUCTION

The study of fluid drops has long been of interest to mathematicians, scientists and engineers (see e.g. References 1–15). In this paper we explore a quasimolecular, i.e. molecular aggregate, approach to modelling liquid drops.[16,17] In particular we will simulate and study large water drops. Our approach will be distinctly different from continuum Navier–Stokes simulations in that we will incorporate classical molecular-type force formulae. Thereby, for example, surface tension will not have to be imposed artificially but will be a direct consequence of the model. CRAY X-MP/24 computer examples will be described and discussed for both stationary and falling drops.

2. MATHEMATICAL, PHYSICAL AND MODELLING PRELIMINARIES

The gross physical response of a fluid to external forces is primarily the result of forces due to gravity and molecular interaction. Gravity acts uniformly on all molecules in a fluid. Molecular interaction forces have components of both attraction and repulsion. Classically, these forces have magnitude F given by

$$F=-\frac{G}{r^p}+\frac{H}{r^q},\quad G>0,\quad H>0,\quad q>p>7, \tag{1}$$

where r is the radius from molecule P to a neighbouring molecule. Because of the singularity in equation (1) at $r=0$, the motion of an individual molecule can be relatively volatile locally, even though the gross motion of the fluid is physically stable.

To simulate fluid motion we will proceed as follows. First we will group the large number of fluid molecules which are physically present into a relatively small number of larger units called quasimolecules or particles. This process of lumping molecules into particles is the same as that utilized by both Boussinesq and Prandtl.[13] Next we define the motion of each particle, denoted by

0271-2091/90/030247-11$05.50

Received March 1988
Revised April 1989

P_i, of the resulting system of, say, N particles by the coupled system of non-linear ordinary differential equations

$$\mathbf{F}_i = m_i \ddot{\mathbf{r}}_i, \quad i = 1, 2, \ldots, N, \tag{2}$$

in which m_i is the mass of P_i. In equation (2),

$$\mathbf{F}_i = \mathbf{F}_{1,i} + \mathbf{F}_{2,i},$$

where $\mathbf{F}_{1,i}$ is the force due to gravity and $\mathbf{F}_{2,i}$ is the force of P_i due to molecular interaction with its neighbours. The force $\mathbf{F}_{1,i}$ applies uniformly to all particles P_i, $i = 1, 2, \ldots, N$. The force $\mathbf{F}_{2,i}$ is determined in accordance with equation (1), but with p and q diminished appropriately in order to maintain the correct gross motion of the system.

Next, the resulting differential system in equation (2) is solved numerically from given initial data as follows.[16] Consider N particles P_i, $i = 1, 2, \ldots, N$. For $\Delta t > 0$ let $t_k = k\Delta t$, $k = 0, 1, 2, \ldots$. For each i let m_i denote the mass of P_i and let P_i at t_k be located at $\mathbf{r}_{i,k} = (x_{i,k}, y_{i,k})$, have velocity $\mathbf{v}_{i,k} = (v_{i,k,x}, v_{i,k,y})$ and have acceleration $\mathbf{a}_{i,k} = (a_{i,k,x}, a_{i,k,y})$. Let position, velocity and acceleration be related by the formulae

$$\mathbf{v}_{i,1/2} = \mathbf{v}_{i,0} + \tfrac{1}{2}(\Delta t)\mathbf{a}_{i,0}, \tag{3}$$

$$\mathbf{v}_{i,k+1/2} = \mathbf{v}_{i,k-1/2} + (\Delta t)\mathbf{a}_{i,k}, \qquad k = 1, 2, \ldots, \tag{4}$$

$$\mathbf{r}_{i,k+1} = \mathbf{r}_{i,k} + (\Delta t)\mathbf{v}_{i,k+1/2}, \qquad k = 0, 1, 2, \ldots. \tag{5}$$

At t_k, let the force acting on P_i be $\mathbf{F}_{i,k} = (F_{i,k,x}, F_{i,k,y})$. We relate force and acceleration by the dynamical equation

$$\mathbf{F}_{i,k} = m_i \mathbf{a}_{i,k}. \tag{6}$$

The motion of each P_i will be determined explicitly and recursively by equations (3)–(6) from given initial data once the force $\mathbf{F}_{i,k}$ is prescribed, and this is done as follows. First fix a positive parameter D, called the distance parameter. We do not exclude the possibility that D is infinite. Any particle P_j, different from P_i, which lies within a circle of radius D and centre P_i is called a neighbour of P_i. If P_j is a neighbour of P_i, let $\mathbf{r}_{ij,k}$ be the vector from P_i to P_j at time t_k, so that $r_{ij,k} = \|\mathbf{r}_{i,k} - \mathbf{r}_{j,k}\|$ is the distance between the two particles. Then the force $\mathbf{F}^*_{ij,k}$ on P_i due to P_j at time t_k is defined by

$$\mathbf{F}^*_{ij,k} = \left(-\frac{G}{(r_{ij,k})^p} + \frac{H}{(r_{ij,k})^q} \right) \frac{\mathbf{r}_{ji,k}}{r_{ij,k}}. \tag{7}$$

The force $\mathbf{F}^*_{i,k}$ on P_i at t_k is defined by

$$\mathbf{F}^*_{i,k} = \sum_{\substack{j=1 \\ j \neq i}} \mathbf{F}^*_{ij,k}, \tag{8}$$

where the summation is taken over all neighbours of P_i. Finally, the total force $\mathbf{F}_{i,k}$ on P_i at t_k is defined by

$$F_{i,k,x} = F^*_{i,k,x}, \quad F_{i,k,y} = F^*_{i,k,y} - m_i g, \tag{9}$$

where g is the constant of acceleration due to gravity.

For the convenience of the reader, a typical CRAY FORTRAN program is available in Greenspan.[10]

3. PARAMETER SELECTION FOR WATER DROPS

For the simulation of water drops by quasimolecules the choices of N, p and q will be dominated by computational considerations, while those of m, G, H and D will be dominated by physical considerations.

For computational convenience and simplicity, set $p = 3$ and $q = 5$. A relatively large time step can then be employed in solving (2). In addition, the computer program will require no square root routine. For budgetary reasons we are limited to $N \sim 1000$ and hence proceed as follows. Consider a rectangular basin of width 2 cm as shown in Figure 1. Into this basin set $N = 1111$ quasimolecules P_i at the respective points (x_i, y_i) determined by

$$x_1 = -1, \quad y_1 = 0, \quad x_{52} = -0{\cdot}98, \quad y_{52} = 0{\cdot}034\,641\,016,$$

$$x_{i+1} = 0{\cdot}04 + x_i, \quad y_{i+1} = y_1, \quad i = 1, 2, \ldots, 50,$$

$$x_{i+1} = 0{\cdot}04 + x_i, \quad y_{i+1} = y_{52}, \quad i = 52, 53, \ldots, 100,$$

$$x_i = x_{i-101}, \quad y_i = 0{\cdot}069\,282\,032 + y_{i-101}, \quad i = 102, 103, \ldots, 1111.$$

The resulting arrangement is shown in Figure 2. The (x_i, y_i) are vertices of a regular triangular mosaic in which the distance from any P_i to an immediate neighbour is 0·04 cm. The height of the system is 0·727 461 33 cm and there are 22 rows of particles which contain, alternately, 51 and 50 particles.

Next, the mass parameter m of each quasimolecule will be determined by mass conservation. For this purpose, suppose that the region filled by quasimolecules, as shown in Figure 2, were to be filled by molecules. Now, for two water molecules, a simplistic potential function $\phi(r)$ is given by[19]

$$\phi(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right], \tag{10}$$

where the distance r between the molecules is in angstroms, $\sigma = 2{\cdot}725$ Å and $\varepsilon = 707$ cal mol^{-1}. Conversion to ergs yields

$$\phi(r) = (1{\cdot}964\,638\,3)\,10^{-13}\left[\left(\frac{2{\cdot}725}{r}\right)^{12} - \left(\frac{2{\cdot}725}{r}\right)^{6}\right] \text{erg}. \tag{11}$$

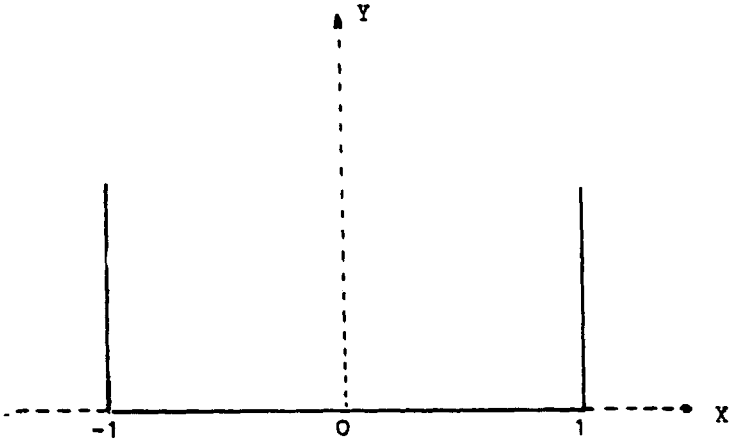


Figure 1. The basin

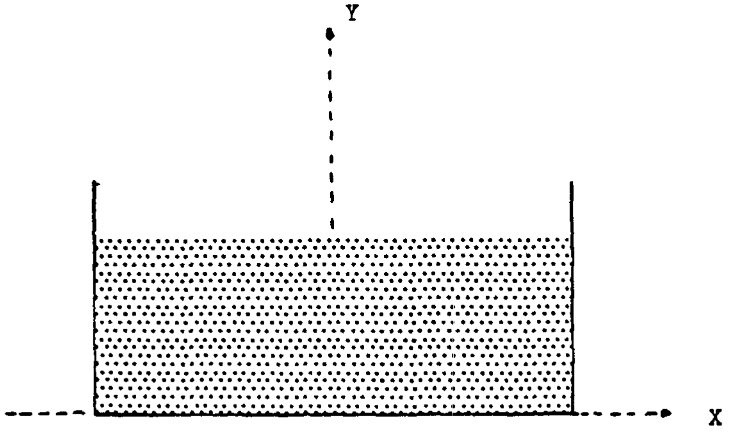


Figure 2. The initial configuration of quasimolecules

Hence

$$F(r) = (1{\cdot}964\,638\,3)\,10^{-5}\left(12\frac{(2{\cdot}725)^{12}}{r^{13}} - 6\frac{(2{\cdot}725)^{6}}{r^{7}}\right)\text{dyn}. \tag{12}$$

Now, when ϕ is a minimum, then $F=0$, which yields

$$\frac{12(2{\cdot}725)^{12}}{r^{13}} - 6\frac{(2{\cdot}725)^{6}}{r^{7}} = 0,$$

the solution of which is

$$r = 3{\cdot}058\,709\ \text{Å}. \tag{13}$$

We now fill the basin up to the height 0·727 461 33 cm with molecules which are also arranged on a regular triangular mosaic, but so that the distance from any molecule to a nearest neighbour is 3·058 709 Å. The generating regular triangle for such a mosaic has edge length 3·058 709 Å and height 2·648 919 6 Å. Since the basin area to be covered is 2 cm by 0·727 461 33 cm, it follows that the number N^* of molecules which fill the area is approximately

$$N^* = \frac{(2)10^8}{3{\cdot}058\,709}\,\frac{(0{\cdot}727\,461\,33)10^8}{2{\cdot}648\,919\,6} = (1.795\,696\,6)10^{15}. \tag{14}$$

Moreover, since the mass of an individual water molecule is $(30{\cdot}103)10^{-24}$ g, the total molecular mass M is approximately

$$M = (5{\cdot}405\,585\,4)10^{-8}\ \text{g}. \tag{15}$$

This total mass is now distributed over the 1111 quasimolecules by the choice

$$m = \frac{(5{\cdot}405\,585\,4)10^{-8}}{1111} = (4{\cdot}865\,513\,4)10^{-11}\ \text{g}. \tag{16}$$

To approximate G and H, consider first the total energy E of the molecular configuration described above. Since E was minimized, the energy is assumed potential. Now, the energy determined by one molecule and any immediate neighbour is, from (11),

$$\phi(3{\cdot}058\,709) = -(4{\cdot}911\,595\,7)10^{-14}\,\text{erg}. \tag{17}$$

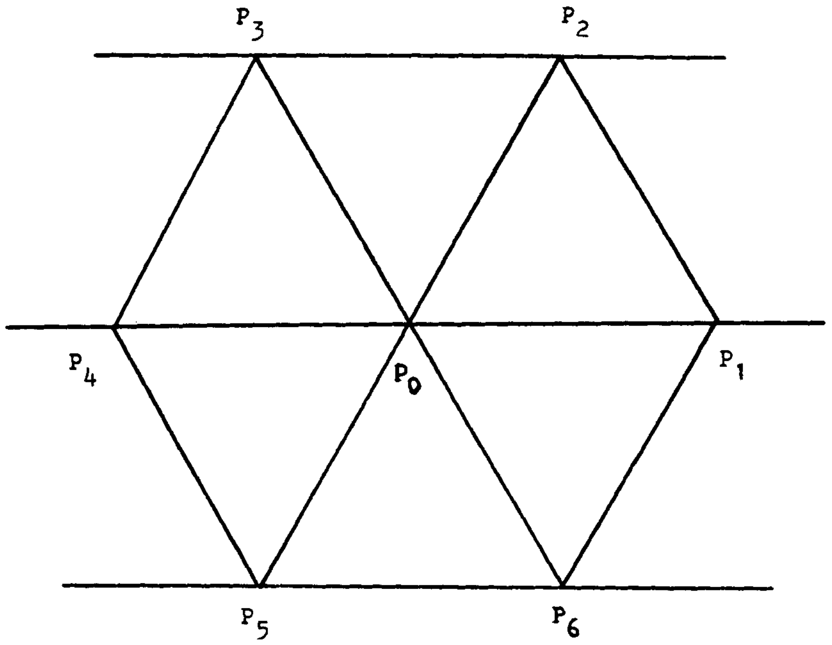


Figure 3. A quasimolecule and its six nearest neighbours

Since the minimum potential results for two such adjacent molecules, we can estimate E as follows. Suppose one traverses the rows of molecules from left to right, starting at the top, and suppose one comes to a particular molecule P_0, as shown in Figure 3. Except at boundary points, P_0 will have exactly six immediate molecular neighbours, which are shown as P_1, P_2, P_3, P_4, P_5 and P_6 in Figure 3. However, the potential energies of the pairs P_0P_2, P_0P_3 and P_0P_4 have already been determined by the method prescribed for traversing the rows. Thus, at P_0, only three contributions are made to the energy calculation and these are for the pairs P_0P_1, P_0P_5 and P_0P_6. Hence from (14) and (17) the total energy is approximately

$$E = 3(1{\cdot}795\,696\,6)10^{15}(-4{\cdot}911\,595\,7)10^{-14}\,\text{erg}$$

or, equivalently,

$$E = -(2{\cdot}645\,920\,7)10^{2}\,\text{erg}. \tag{18}$$

Now, for the quasimolecular system, we have thus far

$$F = -\frac{G}{R^3} + \frac{H}{R^5}\,\text{dyn} \tag{19}$$

with R measured in centimetres. Hence

$$\phi = -\frac{G}{2R^2} + \frac{H}{4R^4}\,\text{erg}. \tag{20}$$

Let us assume that all the energy of the quasimolecular system is also potential. Thus for $R = 0{\cdot}04$ cm it follows that

$$-\frac{G}{(0{\cdot}04)^3} + \frac{H}{(0{\cdot}04)^5} = 0, \tag{21}$$

while conservation of energy implies, from (18), the approximation

$$3(1111)\left(-\frac{G}{2(0{\cdot}04)^2}+\frac{H}{4(0{\cdot}04)^4}\right)=-(2{\cdot}645\,920\,7)10^2. \tag{22}$$

The solution of system (21), (22) is $G=(5{\cdot}080\,675\,8)10^{-4}$, $H=(8{\cdot}129\,081\,2)10^{-7}$, which yields for the quasimolecules the force magnitude

$$F(R)=-\frac{(5{\cdot}080\,675\,8)10^{-4}}{R^3}+\frac{(8{\cdot}129\,081\,2)10^{-7}}{R^5} \tag{23}$$

Unfortunately, force formula (23) is itself unrealistic and requires normalization. This can be seen dynamically by examining force components in the Y-direction only. For, if $\mathbf{R}=(X,Y)$, then (6)–(9) would imply for the motion of quasimolecule P that

$$m\frac{\mathrm{d}^2Y}{\mathrm{d}t^2}=-980m+\sum\left[\left(-\frac{(5{\cdot}080\,675\,8)10^{-4}}{R^3}+\frac{(8{\cdot}129\,081\,2)10^{-7}}{R^5}\right)\frac{Y}{R}\right], \tag{24}$$

where the summation is taken over those quasimolecules which interact with P. However, from (16) it then follows that

$$\frac{\mathrm{d}^2Y}{\mathrm{d}t^2}=-980+\sum\left[\left(-\frac{(1{\cdot}044\,221\,9)10^7}{R^3}+\frac{(1{\cdot}670\,775\,5)10^4}{R^5}\right)\frac{Y}{R}\right], \tag{25}$$

in which the magnitude of the force interaction between quasimolecules is so great that gravity may have no effect at all on any resulting motion. Thus normalization is required and is accomplished appropriately as follows.

In place of (25), consider

$$\frac{\mathrm{d}^2Y}{\mathrm{d}t^2}=-980+\alpha\sum\left[\left(-\frac{(1{\cdot}044\,221\,9)10^7}{R^3}+\frac{(1{\cdot}670\,775\,5)10^4}{R^5}\right)\frac{Y}{R}\right], \tag{26}$$

where α is a normalization constant. Guidance for the choice of α is now derived from actual molecular interaction. In the molecular case the formula (12) is local in the sense that molecules more than five equilibrium distances away from a given molecule have, relative to gravity, a negligible effect on that molecule. We extend this result by assuming that any quasimolecule more than five equilibrium distances away from a given quasimolecule has, relative to gravity, a negligible effect on that quasimolecule. Now, for quasimolecules, the equilibrium distance $\bar{R}$ is, from (23), approximately $\bar{R}=0{\cdot}04$. Hence $6\bar{R}=0{\cdot}24$ and we will determine α in accordance with the inequality

$$\alpha\left|-\frac{(1{\cdot}044\,221\,9)10^7}{(0{\cdot}24)^3}+\frac{(1{\cdot}670\,775\,5)10^4}{(0{\cdot}24)^5}\right|<(1\%)\,(980), \tag{27}$$

from which it follows that $\alpha\sim(1{\cdot}334\,447\,8)10^{-8}$. However, this quantity can be approximated reasonably in terms of constants already developed. Indeed, let Q be the number of molecules which are aggregated into a quasimolecule, so that $Q=N^*/1111$. Then $Q=(1{\cdot}616\,288\,5)10^{12}$ and $1/\sqrt{Q}=(7{\cdot}865\,757\,4)10^{-7}$, which is approximately α. Hence, for simplicity, we set

$$\alpha=1/\sqrt{Q}=\sqrt{\left(\frac{1111}{N^*}\right)}=(7{\cdot}865\,757\,4)10^{-7}, \tag{28}$$

and the magnitude F in (23) is replaced finally by

$$F = (7{\cdot}865\,755\,74)10^{-7}\left(-\frac{(5{\cdot}080\,675\,8)10^{-4}}{R^3} + \frac{(8{\cdot}129\,081\,2)10^{-7}}{R^5}\right)$$

or, more concisely,

$$F = \left(-\frac{3{\cdot}996\,335\,4}{R^3}\,10^{-10} + \frac{6.394\,136\,6}{R^5}\,10^{-13}\right). \tag{29}$$

Finally, since force interactions greater than six times the equilibrium distance are relatively small, we now set the distance parameter D by $D = 2{\cdot}0$. On the CRAY X-MP/24, use of the CFT compiler thereby reduces the computation time to 80% of that required if one uses $D = \infty$.

4. DYNAMICAL EQUATIONS

In the motion of a system of quasimolecules from initial data, it follows from (1), (2) and (29) that the dynamical system to be solved is

$$m\frac{\mathrm{d}^2\mathbf{R}_i}{\mathrm{d}t^2} = -980m\boldsymbol{\delta} + \sum\left[\left(-\frac{3{\cdot}996\,335\,4}{R^3}\,10^{-10} + \frac{6{\cdot}394\,136\,6)}{R^5}\,10^{-13}\right)\frac{\mathbf{R}_{ji}}{R_{ij}}\right], \tag{30}$$

in which $\boldsymbol{\delta} = (0, 1)$ and the summation is taken over all neighbours within a radius of 0·20 cm. However, using (16) and the transformation

$$\mathbf{R} = 0{\cdot}074\,330\,624\,\mathbf{R}^*, \tag{31}$$

$$t = 0{\cdot}027\,263\,643\ T, \tag{32}$$

the equation transforms into

$$\frac{\mathrm{d}^2\mathbf{R}_i^*}{\mathrm{d}T^2} = -9{\cdot}8\,\boldsymbol{\delta} + \sum\left[\left(-\frac{200}{(R_{i,j}^*)^3} + \frac{58}{(R_{i,j}^*)^5}\right)\frac{\mathbf{R}_{j,i}^*}{R_{i,j}^*}\right], \tag{33}$$

which is less sensitive to the choice of time step than is (30). It is (33) which is utilized in the examples to be described next.

5. EXAMPLES

To begin, let us regenerate a basin of quasimolecules which is geometrically similar to that shown in Figure 2 but in the new $\mathbf{R}^* = (X^*, Y^*)$ co-ordinates. We will do this by direct consideration of (33) rather than by applying the transformation (31).

Since

$$-\frac{200}{(R^*)^3} + \frac{58}{(R^*)^5} = 0$$

yields an equilibrium distance of 0·54, let us generate a set of 1111 quasimolecules, as in Section 2, but by the formulae

$$X_1^* = -13{\cdot}75, \quad Y_1^* = 0, \quad X_{52}^* = -13{\cdot}475, \quad Y_{52}^* = 0{\cdot}476\,313\,97,$$

$$X_{i+1}^* = 0{\cdot}55 + X_i^*, \quad Y_{i+1}^* = Y_1^*, \quad i = 1, 2, \ldots, 50,$$

$$X_{i+1}^* = 0{\cdot}55 + X_i^*, \quad Y_{i+1}^* = Y_{52}^*, \quad i = 52, 53, \ldots, 100,$$

$$X_i^* = X_{i-101}^*, \quad Y_i^* = 0{\cdot}952\,627\,94 + Y_{i-101}^*, \quad i = 102, \ldots, 1111.$$

In addition, we will avoid complete symmetry by prescribing small initial velocities, which keep the kinetic energy close to zero, by

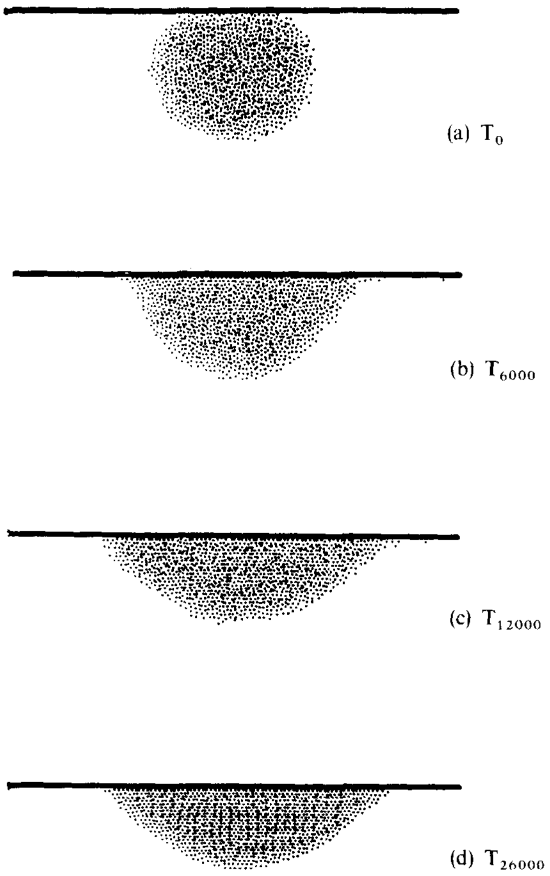
$$\begin{aligned} \mathbf{V}_i^* &= (-0{\cdot}00001, 0{\cdot}0), \quad i = 1, 2, \ldots, 101, \\ \mathbf{V}_i^* &= (0{\cdot}0, \ -0{\cdot}00001,), \quad i = 102, 103, \ldots, 201, \\ \mathbf{V}_i^* &= (0{\cdot}00001, \ -0{\cdot}00001,), \quad i = 202, 203, \ldots, 1111. \end{aligned}$$

We now set $\Delta T = 0{\cdot}0002$, $T_k = k\Delta T$, $k = 0, 1, \ldots$. This time step will be used in all examples to be discussed.

The system of 1111 particles is then allowed to interact in accordance with (33) and the numerical solution is generated using (3)–(5). If any particle collides with a wall of the basin, it is reflected symmetrically but its velocity is damped by the factor 0·8. The interaction distance used is $D = 2{\cdot}75$. The system is allowed to interact through T_{80000}, at which time the fluid particles are reflected about the X-axis, the walls are deleted and a ceiling of 201 additional particles is added by the rule

$$X_i^* = -25{\cdot}0 + (i - 1111)(0{\cdot}25), \quad Y_i^* = 0{\cdot}25, \quad i = 1111, 1112, \ldots, 1312.$$

This result is shown in Figure 4(a).



(a) T_0

(b) T_{6000}

(c) T_{12000}

(d) T_{26000}

Figure 4. Pendent drop formation

The quasimolecules of the ceiling are fixed, i.e. they are not allowed to move, and are called the solid particles. However, they are allowed to interact with the fluid particles with a force effect given by

$$F = -\frac{\bar{G}}{(R^*)^3} + \frac{\bar{H}}{(R^*)^5}. \tag{34}$$

One should observe now that the motions of real fluid drops can take relatively long periods of time.[1] To avoid such a situation we shall choose $\bar{G}$ and $\bar{H}$ in (34) so that fluid adhesion to the ceiling is relatively strong and drop formation relatively rapid. For this reason we set $\bar{G} = 250$ and $\bar{H} = 75$ throughout.

The entire system is now allowed to interact for 6000 time steps, with no imposed damping but with the gravity force decreased from $g = 9{\cdot}8$ to $g = 0{\cdot}98$ to prevent the immediate fall of the fluid from the ceiling. The counter was reset to $T = 0$ and the resulting formation is shown in

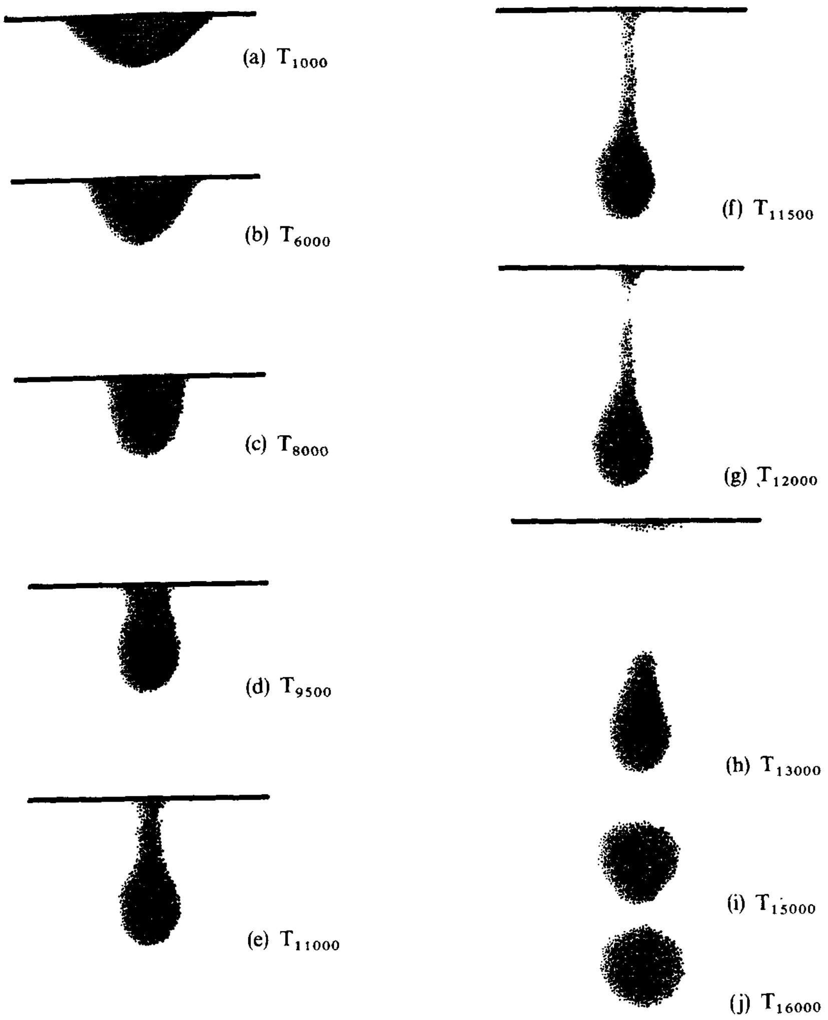


Figure 5. Pendent drop fall


(a) T_{16000} (b) T_{23000}

Figure 6. Trend towards circularization

Figure 4(b) at T_{6000}. The system was then allowed to continue its interaction for 6000 more time steps to T_{12000} but with g reset correctly to 9·8. The result is shown in Figure 4(c). Finally, the system is allowed to interact for an additional 14000 time steps to T_{26000} but with velocities damped initially and every 2000 steps thereafter by the factor 0·2. The result is shown in Figure 4(d). The effect of the damping is to decrease the total kinetic energy or internal heat. The result shown in Figure 4(d) is in complete agreement with experimental shapes of pendent water drops.[7] Moreover, it is worth noting from Figure 4(d) that the fluid quasimolecule at the free surface show a greater separation than do the interior fluid quasimolecules, which is consistent with the theory that it is this relatively large separation in the free surface which manifests itself as surface tension.

Next let us begin with the data for the pendent drop shown in Figure 4(d) and use them as initial data to study the fall of a pendent drop. We again reset the timer. Now the drop shown in Figure 4(d) will not fall of its own accord. Thus it must be dislodged by a suitable force. This can be done in a variety of ways. A computationally convenient way to do this would be simply to increase g, because once the drop has been dislodged its shape will depend only on internal forces, though of course the distance it has fallen will not. Since our primary interest is in the shape of the falling drop, and since again we desire a relatively rapid reaction, we merely take the initial data as that provided by the output for Figure 4(d), eliminate all damping and set g to 98·0. The resulting fall of the drop is shown in Figures 5(a)–(j) at the respective times shown. Figures 6(a) and 6(b) show the shapes of the drop as it continues to fall and indicate its trend towards circularization.

6. REMARKS

In the present paper we have developed a quantitative approach for the simulation of liquid drops. In particular we studied pendent water drops. Previously,[17] such simulations had been strictly qualitative. Our approach utilized molecular aggregates and conservation of mass and energy. The importance of gravity in the study of liquid drop motion, however, required a normalization of the interparticle energy formula. It appears that the methodology would then extend to the study of solids, in those cases where gravity does not play a significant role, without the necessity of normalization.

The examples presented can of course be improved upon. In this first paper we were interested in reasonable results and not in results of the highest precision. Thus in (27) we chose only 1% of the gravity constant to mean 'small with respect to gravity'. We would have made this percentage smaller. In other places also, better choices can now be made. In particular, in retrospect, it probably was not wise to choose the initial velocities $\mathbf{V}_i^*$ as large as they were chosen, since the results are not as symmetrical as experiments indicate. Nevertheless, the results do indicate that, on the actual molecular level, there are oscillations in the free surface.

ACKNOWLEDGEMENT

The computations were performed at the University of Texas Center for High Performance Computing.

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