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SUPERCOMPUTER SIMULATION OF LIQUID DROP FORMATION ON A SOLID SURFACE*

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SUMMARY

Using a molecular-dynamics-type approach, we show how to simulate the formation of a liquid drop on a solid surface. Application is made to the case in which the liquid is water and the solid is graphite. The dynamical equations are large systems of nonlinear, ordinary differential equations which must be solved numerically. CRAY X-MP/24 simulations and related contact angle calculations are described and discussed.

KEY WORDS Liquid drop Molecular model

1. INTRODUCTION

Fluid phenomena which involve large gradients present exceptional theoretical difficulties.[1] This is readily apparent in the study of liquid drops, in which surface tension plays a major role.[2-4] In this paper we will develop a molecular-dynamics-type approach to such problems. In particular, we will show how to simulate the formation of a liquid drop, taken to be water, on a horizontal solid surface, taken to be graphite. The related dynamical equations will be large systems of second-order, non-linear, ordinary differential equations which will be solved numerically[5] on a CRAY X-MP/24. Since our numerical method will require minimal memory but maximal 'number-smashing' capabilities, the CRAY is a most convenient computer to use, since on it we will be able to solve our 1003 equations for 4000 time steps in 97 s.

At present, for budgetary reasons and for computational simplicity, attention will be restricted to two-dimensional simulations. Nevertheless, all the ideas and methods do extend to three dimensions.[6]

2. LOCAL FORCE FORMULAE

In order not to be confined to a system of molecules whose volume is prohibitively small,[7] we will think in terms of aggregates of molecules, called particles or quasi-molecules. The force interaction formulae for particles will be derived in this section by conserving the total mass and the total energy of the original molecular system.

Consider first the system of 823 water particles $P_1, P_2, \ldots, P_{823}$ shown in Figure 1. These particles are arranged on a regular triangular mosaic but in a relatively circular pattern. The edge length of each triangle in the mosaic is 0·030 5871 cm, the rationale of which will be explained shortly. The algorithm for generating the positions $\mathbf{r}(i)=(x(i), y(i))$ and velocity $\mathbf{v}(i)=(v_x(i),$

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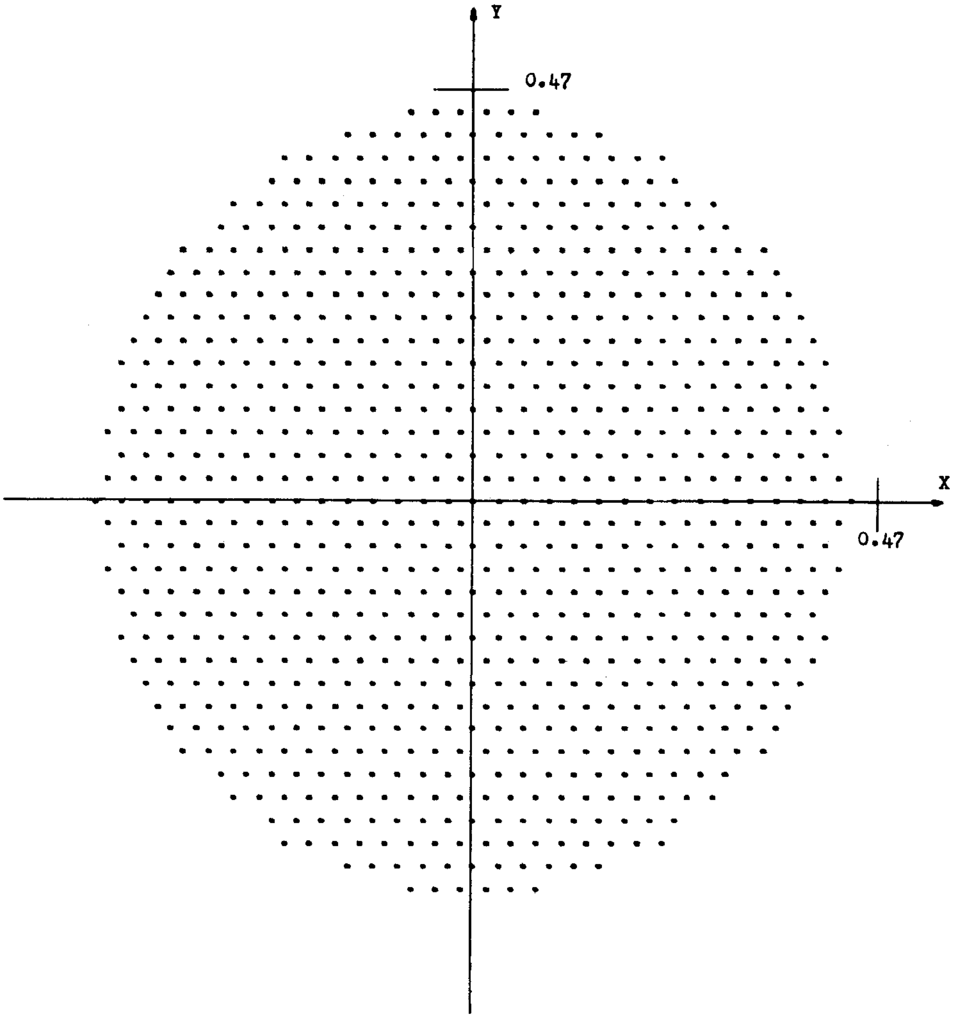

Figure 1. Initial fluid

$v_y(i)$) for each P_i is given as follows. From the 9500 points with

$$x(1)=-0{\cdot}6117420,\quad y(1)=-0{\cdot}7946762,\quad v_x(1)=0{\cdot}0,\quad v_y(1)=10^{-9},$$

$$x(42)=-0{\cdot}5964485,\quad y(42)=-0{\cdot}7681870,\quad v_x(42)=10^{-9},\quad v_y(42)=0{\cdot}0,$$

$$x(i+1)=x(i)+0{\cdot}0305871,\quad y(i+1)=y(1),\quad v_x(i+1)=0{\cdot}0,\quad v_y(i+1)=v_y(1),$$

$$i=1, 2, 3, \dots, 40,$$

$$x(i+1)=x(i)+0{\cdot}0305871,\quad y(i+1)=y(42),\quad v_x(i+1)=v_x(42),\quad v_y(i+1)=0{\cdot}0,$$

$$i=42, 43, \dots, 80,$$

$$x(i)=x(i-81),\quad y(i)=y(i-81)+0{\cdot}0529784,\quad v_x(i)=-v_x(i-81),\quad v_y(i)=-v_y(i-81),$$

$$i=82, 83, \dots, 9500,$$

choose only those which satisfy

$$[x(i)]^2+[y(i)]^2 \leqslant 0{\cdot}2123. \tag{1}$$

These are the 823 points shown in Figure 1. Note that the horizontal radius of this relatively circular set contains 15 particles, so that the radius r is approximately

$$r=15(0{\cdot}0305871)=0{\cdot}4588065 \text{ cm}. \tag{2}$$

For the interaction of the particles we assume a force $\mathbf{F}_1$, in dynes, between two particles R cm apart, with magnitude F_1 given

$$F_1(R)=-\frac{G}{R^3}+\frac{H}{R^5}. \tag{3}$$

From (3) then, in ergs,

$$\phi_1(R)=-\frac{G}{2R^2}+\frac{H}{4R^4}. \tag{4}$$

For the system shown in Figure 1 we assume that $F_1=0$ between two neighbours, so that

$$-(0{\cdot}0305871)^2G+H=0. \tag{5}$$

Assuming zero kinetic energy, the total energy E_1 of the particle system is approximately[4]

$$E_1=3(823)\left(-\frac{G}{2(0{\cdot}0305871)^2}+\frac{H}{4(0{\cdot}0305871)^4}\right). \tag{6}$$

We show next how to use (5), (6) and conservation of total energy to determine G and H uniquely in (3). For actual water molecules one can use the approximation[8]

$$\phi(r)=(1{\cdot}9646383)10^{-13}\left[\left(\frac{2{\cdot}725}{r}\right)^{12}-\left(\frac{2{\cdot}725}{r}\right)^{6}\right]\text{erg}, \tag{7}$$

in which the distance r between two molecules is measured in angstroms. From (7) the magnitude of the force $\mathbf{F}$, in dynes, is

$$F(r)=(1{\cdot}9646383)10^{-5}\left(12\frac{(2{\cdot}725)^{12}}{r^{13}}-6\frac{(2{\cdot}725)^6}{r^7}\right). \tag{8}$$

Note from (8) that $F(r)=0$ implies $r=3{\cdot}05871$ Å. (Our choice of 0·0305871 cm for the construction of Figure 1 was based on this angstrom measurement for the purpose of simplifying later calculations.) We now fill the circle shown in Figure 1 with molecules which are vertices of a regular triangular grid with edge length 3·05871 Å. The number N of molecules which fill the region is approximately

$$N=\pi\left(\frac{15(0{\cdot}0305871)}{(3{\cdot}05871)10^{-8}}\right)^2\approx(706{\cdot}858)10^{12}. \tag{9}$$

Assuming zero kinetic energy, the total energy E of the molecular system is approximately

$$E=3(707)10^{12}(1{\cdot}9646383)10^{-13}\left[\left(\frac{2{\cdot}725}{3{\cdot}05871}\right)^{12}-\left(\frac{2{\cdot}725}{3{\cdot}05871}\right)^{6}\right]\text{erg} \tag{10}$$

or

$$E=-104{\cdot}1745.$$

Note that the expression in the square brackets of (10) is simply $[(\frac{1}{2})^2-(\frac{1}{2})]$. Equating E_1 and E implies

$$-534{\cdot}4332\,G+285618{\cdot}8\,H=-0{\cdot}04219299. \tag{11}$$

The solution of (5) and (11) is

$$G=(1{\cdot}57898)\,10^{-4}, \qquad H=(1{\cdot}47725)\,10^{-7},$$

so that (3) and (4) can be given explicitly as

$$F_1(R)=-\frac{1{\cdot}57898}{R^3}\,10^{-4}+\frac{1{\cdot}47725}{R^5}\,10^{-7}, \tag{12}$$

$$\phi_1(R)=-\frac{7{\cdot}8949}{R^2}\,10^{-5}+\frac{3{\cdot}693125}{R^4}\,10^{-8}. \tag{13}$$

Note that (13) can be rewritten in the form

$$\phi_1(R)=4\varepsilon_1\left[-\left(\frac{\sigma_1}{R}\right)^2+\left(\frac{\sigma_1}{R}\right)^4\right], \tag{14}$$

in which $\varepsilon_1=0{\cdot}0421929$ and $\sigma_1=0{\cdot}0216284$.

Note also that since the mass of a single water molecule is approximately $m=(30{\cdot}103)\,10^{-24}$ g, distributing the total water molecule mass over the 823 particles yields an individual water particle mass M_1 given by

$$M_1=(2{\cdot}586)\,10^{-11}\ \text{g}. \tag{15}$$

Using the very same line of reasoning as for water, let us proceed to develop appropriate formulae for graphite. A five-row, 1003-particle slab of graphite particles is generated using a regular triangular mosaic with edge length 0·03834 cm by the formulae

$$x(1)=-3{\cdot}834,\quad y(1)=0{\cdot}0,\quad x(202)=-3{\cdot}81085,\quad y(202)=0{\cdot}03317,$$

$$x(i+1)=x(i)+0{\cdot}03834,\quad y(i+1)=y(1),\qquad i=1,2,\ldots,200,$$

$$x(i+1)=x(i)+0{\cdot}03834,\quad y(i+1)=y(202),\qquad i=202,203,\ldots,400,$$

$$x(i)=x(i-401),\quad y(i)=0{\cdot}06634+y(i-401),\qquad i=402,403,\ldots,1003.$$

The resulting slab is 7·688 cm wide and 0·13268 cm high, and is shown in Figure 2. One should note immediately the difference in units between Figures 1 and 2.

Let the force $\mathbf{F}_2$, in dynes, between two graphite particles R cm apart have magnitude F_2 given by

$$F_2(R)=-\frac{G}{R^3}+\frac{H}{R^5}, \tag{16}$$

Figure 2. Initial slab

so that

$$\phi_2(R) = -\frac{G}{2R^2} + \frac{H}{4R^4}. \tag{17}$$

Assuming $F_2 = 0$ for two neighbours, (16) implies, in analogy with (5),

$$-(0{\cdot}03834)^2 G + H = 0. \tag{18}$$

Assuming zero kinetic energy, the total energy E_2 of the system is approximately

$$E_2 = 3(1003)\left(-\frac{G}{2(0{\cdot}03834)^2} + \frac{H}{4(0{\cdot}03834)^4}\right). \tag{19}$$

However, for actual atoms of graphite,[9, 10] with r in angstroms,

$$\phi(r) = \left(\frac{38591{\cdot}3}{r^{12}} - \frac{24{\cdot}3000}{r^6}\right) 10^{-12}\ \text{erg}, \tag{20}$$

$$F(r) = \left(\frac{463095{\cdot}6}{r^{13}} - \frac{145{\cdot}8}{r^7}\right) 10^{-4}, \tag{21}$$

where $\mathbf{F}(r)$ is measured in dynes. In (20) and (21), $\phi(3{\cdot}41570) = 0$ and $F(3{\cdot}83400) = 0$. Then the number N of atoms which fill the slab on a regular triangular mosaic with edge length 3·83400 Å is

$$N = \frac{(7{\cdot}668)\,10^8}{3{\cdot}83400}\,\frac{(0{\cdot}13268)\,10^8}{3{\cdot}3203483} = (7{\cdot}992)\,10^{14}.$$

Assuming zero kinetic energy, the total energy E of the system is approximately

$$E = 3(7{\cdot}992)\,10^{14}\left(\frac{38591{\cdot}3}{(3{\cdot}83400)^{12}} - \frac{24{\cdot}3000}{(3{\cdot}83400)^6}\right) 10^{-12}, \tag{22}$$

so that $E = -9{\cdot}17149$. Note that the ratio of the numbers in the large parentheses of (22) is two. Equating E and E_2 implies

$$-\frac{G}{2(0{\cdot}03834)^2} + \frac{H}{4(0{\cdot}03834)^4} = -(3{\cdot}04802)\,10^{-3} \tag{23}$$

The solution of system (18) and (23) is approximately

$$G = (1{\cdot}792181)\,10^{-5} \quad \text{and} \quad H = (2{\cdot}634426)\,10^{-8}$$

Thus

$$F_2 = -\frac{1{\cdot}792181}{R^3}\,10^{-5} + \frac{2{\cdot}634426}{R^5}\,10^{-8}, \tag{24}$$

$$\phi_2 = -\frac{8{\cdot}960905}{R^2}\,10^{-6} + \frac{6{\cdot}586065}{R^4}\,10^{-9}. \tag{25}$$

Note that $\phi_2(0{\cdot}0271105) = 0$, so that ϕ_2 can be rewritten as

$$\phi_2 = 4\varepsilon_2\left[-\left(\frac{\sigma_2}{R}\right)^2 + \left(\frac{\sigma_2}{R}\right)^4\right], \tag{26}$$

in which $\sigma_2 = 0{\cdot}271105$ and $\varepsilon_2 = (3{\cdot}048013)\,10^{-3}$.

Note that since the mass of a carbon atom is approximately $(1{\cdot}9938)10^{-23}$ g, the total atomic mass of the slab, when distributed over the 1003 graphite particles, yields a particle mass M_2 given by

$$M_2=(1{\cdot}588679)10^{-11}\text{ g.} \tag{27}$$

Finally, to determine the force $\mathbf{F}_3$ between graphite and water particles, we use the empirical bonding law[4]

$$\phi_3=4\varepsilon_3\left[\left(\frac{\sigma_3}{R}\right)^4-\left(\frac{\sigma_3}{R}\right)^2\right],$$

where $\varepsilon_3=\surd(\varepsilon_1\varepsilon_2)=0{\cdot}0113404$ and $\sigma_3=\frac{1}{2}(\sigma_1+\sigma_2)=0{\cdot}02436945$. Thus

$$\phi_3=-\frac{2{\cdot}6938}{R^2}10^{-5}+\frac{1{\cdot}5998}{R^4}10^{-8}.$$

Hence

$$F_3=-\frac{5{\cdot}3877}{R^3}10^{-5}+\frac{6{\cdot}3992}{R^5}10^{-8}. \tag{28}$$

In summary, the water–water interparticle force $\mathbf{F}_1$, graphite–graphite interparticle force $\mathbf{F}_2$ and water–graphite interparticle force $\mathbf{F}_3$ yield, to four significant figures,

$$F_1(R)=-\frac{1{\cdot}579}{R^3}10^{-4}+\frac{1{\cdot}477}{R^5}10^{-7}, \tag{29}$$

$$F_2(R)=-\frac{1{\cdot}792}{R^3}10^{-5}+\frac{2{\cdot}634}{R^5}10^{-8}, \tag{30}$$

$$F_3(R)=-\frac{5{\cdot}388}{R^3}10^{-5}+\frac{6{\cdot}399}{R^5}10^{-8}, \tag{31}$$

while

$$F_1(0{\cdot}03059)=F_2(0{\cdot}03834)=F_3(0{\cdot}03446)=0. \tag{32}$$

The distances $R_1=0{\cdot}03059$, $R_2=0{\cdot}03834$ and $R_3=0{\cdot}03446$ are called equilibrium radii.

3. DYNAMICAL EQUATIONS

In order to derive dynamical equations for particle motions, let us begin with the motion of a water particle P_i as it interacts with other water particles. The motion of P_i, in general, is given by

$$M_1\frac{\mathrm{d}^2R_i}{\mathrm{d}t^2}=-980\,M_1+\alpha_1\sum_j\left(-\frac{1{\cdot}579}{(R_{ij})^3}10^{-4}+\frac{1{\cdot}477}{(R_{ij})^5}10^{-7}\right), \tag{33}$$

in which the summation is taken over particles P_j which are within a prescribed distance D_1 from P_i, R_{ij} is the distance between P_i and P_j, α_1 is a scaling factor which assures that the particle interaction is local relative to gravity, and M_1 is the mass of a water particle given by (15). Division by M_1 yields

$$\frac{\mathrm{d}^2R_i}{\mathrm{d}t^2}=-980+\alpha_1\sum_j\left(-\frac{0{\cdot}61060}{(R_{ij})^3}10^{7}+\frac{0{\cdot}57115}{(R_{ij})^5}10^{4}\right). \tag{34}$$

We now assume, as is common in molecular mechanics, that P_i is acted upon only by particles P_j which are within five equilibrium radii of P_i, so that $D_1 = 5(0{\cdot}03059) = 0{\cdot}15295$. By 'local relative to gravity' we assume the usual 5% experimental error allowance, so that

$$\alpha_1\left|-\frac{(0{\cdot}61060)}{(0{\cdot}15295)^3}10^7+\frac{(0{\cdot}57115)}{(0{\cdot}15295)^5}10^4\right| = 5\%(980),$$

which yields $\alpha_1 = (2{\cdot}99095)10^{-8}$. Thus (34) reduces to

$$\frac{d^2R_i}{dt^2} = -980 + \sum_j\left(-\frac{1{\cdot}82627}{(R_{ij})^3}10^{-1}+\frac{1{\cdot}70828}{(R_{ij})^5}10^{-4}\right). \tag{35}$$

Finally, making the changes of varibles

$$\bar{R} = 10R, \qquad T = 10t, \tag{36}$$

(35) reduces to

$$\frac{d^2\bar{R}_i}{dT^2} = -98{\cdot}0 + \sum_j\left(-\frac{18{\cdot}2627}{(\bar{R}_{ij})^3}+\frac{1{\cdot}70828}{(\bar{R}_{ij})^5}\right). \tag{37}$$

Using the same line of reasoning, the dynamical equation for the interaction of a graphite particle with other graphite particles is

$$\frac{d^2R_i}{dt^2} = -980 + \sum_j\left(-\frac{0{\cdot}359575}{(R_{ij})^3}+\frac{5{\cdot}285275}{(R_{ij})^5}10^{-4}\right), \tag{38}$$

and the distance of local interaction is $D_2 = 0{\cdot}1917$. Under transformations (36) the equation becomes

$$\frac{d^2\bar{R}_i}{dT^2} = -98{\cdot}0 + \sum_j\left(-\frac{35{\cdot}9575}{(\bar{R}_{ij})^3}+\frac{5{\cdot}285275}{(\bar{R}_{ij})^5}\right). \tag{39}$$

The interaction of a water particle P_i with graphite particles P_j is governed by the equation

$$\frac{d^2R_i}{dt^2} = -980 + \sum_j\left(-\frac{0{\cdot}261085}{(R_{ij})^3}+\frac{3{\cdot}10075}{(R_{ij})^5}10^{-4}\right), \tag{40}$$

with the local interaction distance $D_3 = 0{\cdot}1723$. Under transformations (36), the equation becomes

$$\frac{d^2\bar{R}_i}{dT^2} = -98{\cdot}0 + \sum_j\left(-\frac{26{\cdot}1085}{(\bar{R}_{ij})^3}+\frac{3{\cdot}10075}{(\bar{R}_{ij})^5}\right). \tag{41}$$

Note, incidentally, that the first transformation in (36) has the effect of multiplying all co-ordinates in Figures 1 and 2 by the factor 10. Hereafter, all discussion is in terms of variables $\bar{R}$ and T. However, the random initial velocities prescribed for particles P_1–P_{823} will be retained.

4. DROP AND SLAB STABILIZATION

If, for example, one proceeds numerically with $\Delta T = 0{\cdot}00005$ and one allows the water particles to interact in accordance with (37), the system exhibits large expansion and contraction modes. The reason is that the initial potential energy is large. To overcome this situation, P_1–P_{823} were allowed to interact in accordance with (37), but every 1000 time steps all velocities were damped by the factor 0·9. At the end of 37000 time steps the damping was removed and the particles were allowed to interact for 9000 more time steps to t_{46000}. The large oscillating modes were no longer

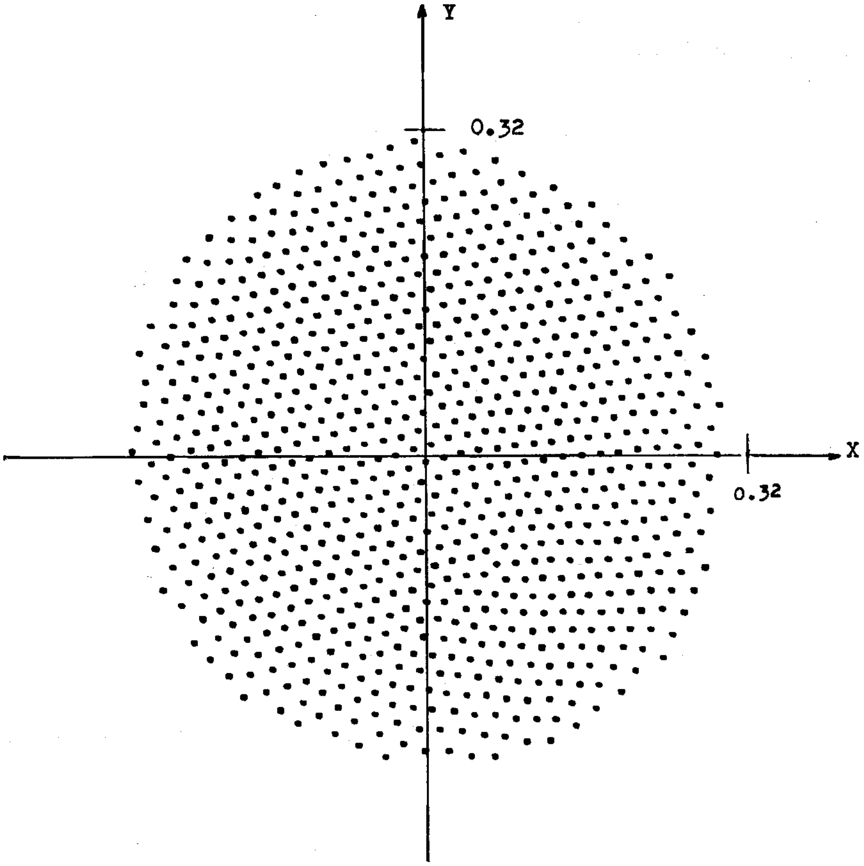

Figure 3. Stable fluid

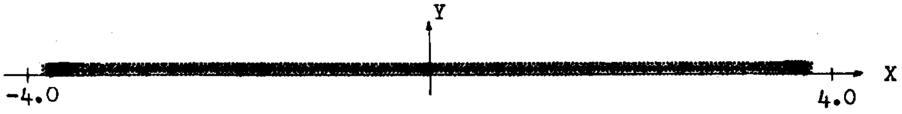

Figure 4. stable slab

present. The resulting stable configuration is shown in Figure 3, where, most importantly, the outermost particles show a lower density than the inner particles, which is characteristic of liquid surface tension. The average diameter in Figure 3 is appoximately two-thirds that of Figure 1.

The slab was stabilized in accordance with (39), but in the following fashion in order to maintain its solid state. Again we chose $\Delta T = 0{\cdot}00005$. Whenever the total system kinetic energy exceeded 100, all velocities were damped by the factor 0·25. The system was allowed to run to t_{25000}, at which time the slab had contracted vertically primarily to the relatively stable configuration shown in Figure 4. More extensive time calculations led to crumbling, which was

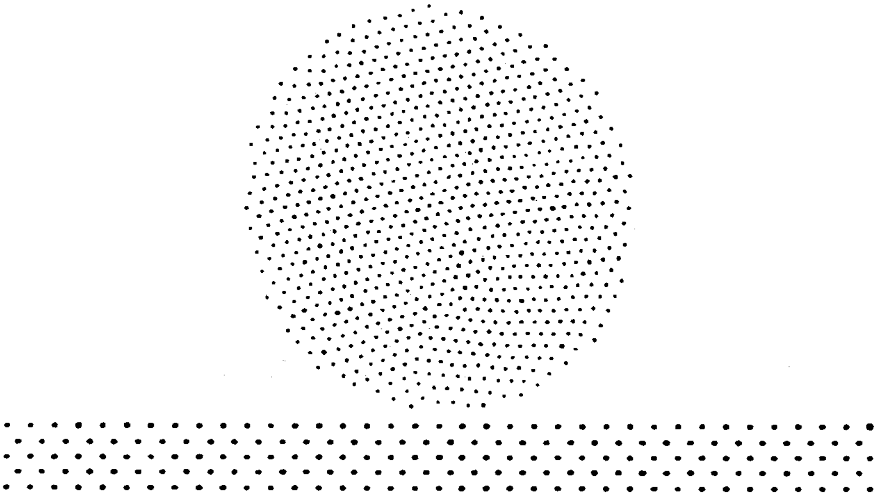

Figure 5. $T=0{\cdot}0$

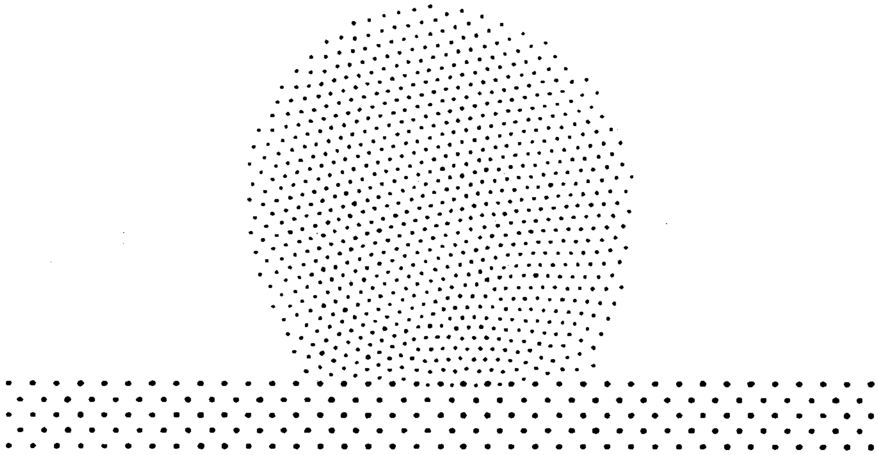

Figure 6. $T=0{\cdot}28$, KE=4500

considered to be physically unreasonable. The result in Figure 4 has a height which is approximately two-thirds of that shown in Figure 2.

5. SESSILE DROP FORMATION

The drop shown in Figure 3 is now translated vertically upwards 4·5 units so that it sits immediately above the slab shown in Figure 4. This arrangement is shown in Figure 5, with only the central slab particles being plotted. The mode of presentation in this and the next graphs distinguishes between the water and carbon particles so that the interaction can be discerned easily.

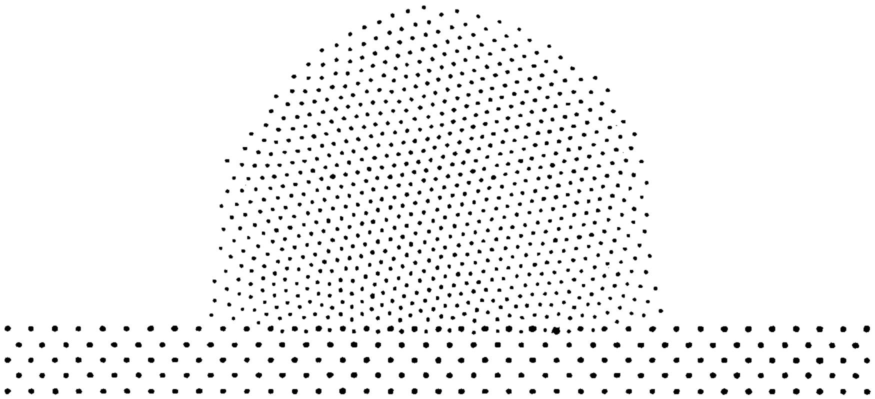

Figure 7. $T=0{\cdot}60$, KE = 1900

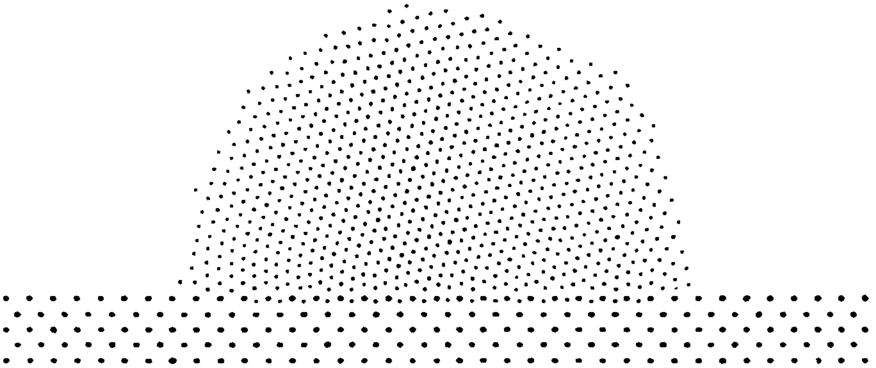

Figure 8. $T=0{\cdot}92$, KE = 840

The slab particles were allowed no further motion, but P_1-P_{823} were allowed to interact with themselves and with the graphite particles in accordance with (37) and (39). For the first 200000 steps of the computer simulation we used $\Delta T=1(10^{-6})$. Thereafter we used $\Delta T=2(10^{-6})$. To account for the energy increase due to the effect of gravity, all velocities were damped by 0·9 every 2000 time steps all through the calculations. This was not considered to be significant since our interest was only a relatively steady state configuration.

The results are summarized in Figures 6–9 at the respective times $T=0{\cdot}28$, 0·60, 0·92 and 1·40. The kinetic energy KE is also recorded in each caption since it reflects the temperature of the system. The figures show an interlocking of particles below the central fluid mass and a relative steady state at $T=1{\cdot}40$. Using linear least square approximations with the four lowest boundary particles on the left and right sides of the system, as shown in Figure 10, we found a left contact angle of 64° and a right contact angle of 68°, the average being 66°. An experimentally determined contact angle measurement reported[1] is 60°.

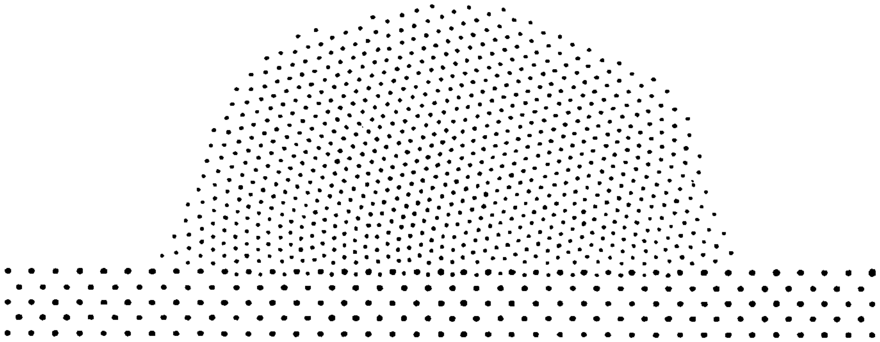

Figure 9. $T=1{\cdot}40$, $\mathrm{KE}=85$

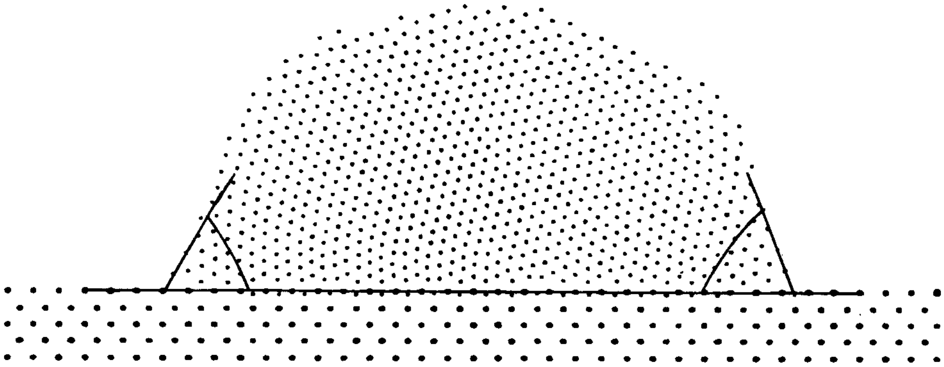

Figure 10. Contact angle fit

6. REMARKS

Improvement in the results reported here should follow as the numbers of water and graphite particles are increased and the interaction parameters are made more precise.

The problem of determining the temperature through the kinetic energy remains, since no precise connecting relationship is available for quasi-molecular systems as exists for molecular systems.

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