Chapter 1

Quasimolecular Modelling: What It Is and What It Is Not

1.1. Introduction

Science is the study of Nature. We study Nature not only because we are curious, but because we would like to control its very powerful forces. Understanding the ways in which Nature works might enable us to grow more food, to prevent normal cells from becoming cancerous, and to develop relatively inexpensive sources of energy. In cases where control may not be possible, we would like to be able to predict what will happen. Thus, being able to predict when and where an earthquake will strike might save lives, even though, at present, we have no expectation of being able to prevent a quake itself.

The discovery of knowledge by scientific means is carried out in the following way. First, there are experimental scientists who, as meticulously as possible, reach conclusions from experiments and observations. Since experimental conditions can never be reproduced exactly, and since no one is perfect, not even a scientist, all experimental conclusions have some degree of error. Hopefully, the error will be small. Then there are the theoretical scientists, who create models from which conclusions are reached, often using mathematical methods. Experimental scientists are constantly checking these models by planning and carrying out new experiments. Theoreticians are constantly refining their models by incorporating new experimental results. The two groups work in a constant check-and-balance refinement process to create knowledge. And only after extensive experimental verification and widespread professional agreement is a scientific conclusion accepted as valid.

Our concern in this book is with a new area of theoretical modelling which is called *quasimolecular modelling*, or more succinctly, *Q modelling*, or, less precisely, *particle modelling*. Though specifics will follow in later sections, we observe now, for the purpose of providing an overview, that quasimolecular modelling is the study of the dynamical behavior of solids and fluids in response to external forces, the solids and fluids being modelled as systems of molecules or molecular aggregates, which interact in a fashion entirely analogous to classical Newtonian molecular interaction. The dynamical equations of Q modelling are large systems of second order, nonlinear, ordinary differential equations.

Note that for linguistic simplicity, the term *molecule* will be used throughout as a generic term which includes both *atom* and *molecule*.

The primary differences between *quasimolecular modelling* and *molecular mechanics* modelling (Alder and Wainwright (1960); Hoover (1984)) can be describe as follows. The field of statistical mechanics combines the rules of statistics with the laws of Newtonian mechanics to describe quantitative, large scale properties of continuous solids and fluids from the most probable behavior of constituent molecules. Primary goals of statistical mechanics are the derivation of macroscopic thermodynamic properties relating to such quantities as temperature, stress, internal energy, and heat flow, and the derivation of equations of state which relate pressure, energy, volume and temperature. *Molecular mechanics* modelling is a computer approach applied directly to a small molecular subset of a given substance with the objective of confirming or modifying large scale statistical mechanics properties or equations. The major results in molecular mechanics have been equilibrium, that is, steady state, results. Q modelling, on the other hand, is concerned, primarily, with nonsteady state phenomena and with variations in dynamical response due to variation of system parameters. In addition, Q modelling applies both to sets of molecules and to sets of molecules which have been aggregated into larger units called quasimolecules. It is through quasimolecular systems that Q modelling can be made to simulate exorbitantly large systems of molecules.

For linguistic ease, we will often use the term *particle* rather than *quasi-*

molecule. However, it must be noted that this usage of the term *particle* is different from the usage of others. Buneman *et al.* (1980) and Hockney and Eastwood (1981) use the term *particle* to represent an ion in a plasma. Amsden (1966) and Harlow and Sanmann (1965) use the term to represent a fluid point of positive mass which moves in accordance with mass, energy and momentum conservation properties which are incorporated in a system of partial differential equations in two space dimensions.

In the present context, the term *particle* will always mean an aggregate of molecules.

1.2. Classical Molecular Forces

From the classical, Newtonian point of view, both atoms and molecules exhibit the following behavior. Two molecules, for example, interact only locally, that is, when they are in close proximity to each other. Qualitatively, this interaction is of the following character (Feynman, Leighton and Sands (1963)). If pushed together, the molecules repel; if pulled apart they attract; and the repulsive force is of a greater order of magnitude than is the attractive one. A mathematical formulation of the behavior can be given as follows (Hirshfelder, Curtiss and Bird(1954)).

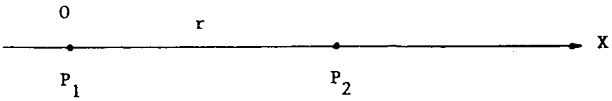


Fig. 1.1.

Consider two molecules P_1 and P_2 on an X-axis, as shown in Fig. 1.1. Let P_1 be at the origin and let P_2 be at a positive distance r from P_1. Let the force $\mathbf{F}$ which P_1 exerts on P_2 have magnitude F given by

$$F = -\frac{G}{r^p} + \frac{H}{r^q} , \tag{1.1}$$

where G, H, p, q are positive constants with $q > p$. Consider, for example, $G = H = 1, p = 6, q = 12$, which are good approximations for a variety of experimental results (Hirschfelder, Curtiss and Bird (1954)). Then

$$F = -\frac{1}{r^6} + \frac{1}{r^{12}} . \tag{1.2}$$

If, in (1.2), $r = 1$, then $F = 0$, so that P_1 exerts no force on P_2. In this case, one says that the molecules are in equilibrium. If $r > 1$, say $r = 2$, then

$$F = -\frac{1}{2^6} + \frac{1}{2^{12}} , \tag{1.3}$$

which is negative, so that P_1 exerts an attractive force on P_2. If, on the other hand, $0 < r < 1$, say, $r = 0.1$, then

$$F = -\frac{1}{(0.1)^6} + \frac{1}{(0.1)^{12}} , \tag{1.4}$$

which is positive, so that P_1 exerts a repulsive force on P_2. As r approaches zero, the force F in (1.2) becomes unbounded in magnitude. Mathematically, r is not allowed to be zero because, if it were, F in (1.2) would be undefined. Physically, r is not allowed to be zero because one assumes conservation of mass, so that the same position cannot be occupied simultaneously by different physical entities. If one sets $F = 0$ in (1.1), then, using the reasoning above for (1.2), one finds that equilibrium results if

$$r = \left(\frac{H}{G}\right)^{\frac{1}{(q-p)}} , \tag{1.5}$$

with an attractive force resulting for larger values of r and a repulsive force for smaller ones.

It is important to observe that even though the gross motion of, for example, a fluid may be physically stable, the motion between two neighboring molecules of the fluid, in accordance with (1.1), may be highly volatile. This volatility, however, is strictly local.

1.3. General Modelling Principles

To simulate the dynamical response of a solid or fluid to external forces, we will proceed in general as follows. First, we will group the large number of molecules physically present into a smaller number of subunits called quasimolecules or particles. In the case of fluids, for example, this aggregation process is exactly the same as that utilized by both Boussinesq (1913) and Prandtl (1925). Assume, then, that the number of particles which results is N. Denote these by $P_i, i = 1, 2, \ldots, N$ and let the mass of P_i be m_i. From given initial data, the motion of each P_i is then prescribed by the coupled system of ordinary differential equations:

$$\mathbf{F}_i = m_i \ddot{\mathbf{r}}, \qquad i = 1, 2, \ldots, N , \tag{1.6}$$

in which $\mathbf{F}_i$ is the force on P_i, $\mathbf{r}_i$ is the position vector of P_i, and differentiation is with respect to time. In (1.6), we assume that

$$\mathbf{F}_i = \mathbf{F}_i^{**} + \mathbf{F}_i^{*} \ , \tag{1.7}$$

where $\mathbf{F}_i^{**}$ is an external or long range force, which, like gravity, can act on all the particles uniformly or, like a driving force, can act on a particular subset of the particles; and $\mathbf{F}_i^{*}$ is the local, short range force on P_i due to molecular type interaction with its immediate neighbors. In practice, a positive parameter D, called the ***distance of local interaction parameter***, will often be associated with $\mathbf{F}_i^{*}$. It will assure that $\mathbf{F}_i^{*}$ is, in fact, local by only allowing particles whose distance to P_i is less than D to have a nonzero effect on P_i. Hence, D can be viewed as a switching parameter which turns off $\mathbf{F}_i^{*}$ for all paricles except those close to P_i.

Observe that when a substance under consideration has, approximately, 10^{22} molecules, then a choice of N in the range $10^2 \leq N \leq 10^4$ yields a relatively small number of particles. For such choices of N, parameter choices like $p = 6, q = 12, G = H = 1$ in (1.1), which are realistic for systems of molecules, are not realistic for systems of particles, since local volatility will then also yield system volatility. In order to insure the physical stability of a system of particles, it will be necessary then to decrease the exponents p and q appropriately. Thus, molecular type attraction and repulsion will be incorporated in Q modelling, but with decreased local volatility in order to assure physical stability of the system.

1.4. Numerical Solution

In general, system (1.6) cannot be solved analytically from given initial data and must be solved numerically. The choice of a numerical method is simplified by the fact that the physics of Q modelling demands small time steps. The reason is that only with small time steps can the repulsive component H/r^q in (1.1) be treated accurately for small r, since H/r^q is unbounded as r goes to zero. Thus, the advantages in using high-order numerical methods, which allow the choice of large time steps in obtaining high-order accuracy, are not applicable in Q modelling. Hence, for economy, simplicity, and relative numerical stability, we will utilize the leap-frog formulae (Greenspan (1980a)), which are described as follows.

For positive time step Δt, let $t_k = k\Delta t, k = 0, 1, 2, \ldots$. For $i = 1, 2, \ldots, N$, let P_i have mass m_i and at t_k let P_i be located at $\mathbf{r}_{i,k}$, have velocity $\mathbf{v}_{i,k}$ and have acceleration $\mathbf{a}_{i,k}$. Then the leap-frog formulae, which relate position, velocity and acceleration are

$$\mathbf{v}_{i,1/2} = \mathbf{v}_{i,0} + \frac{(\Delta t)}{2}\mathbf{a}_{i,0}\,, \qquad \text{(starter formula)} \tag{1.8}$$

$$\mathbf{v}_{i,k+1/2} = \mathbf{v}_{i,k-1/2} + (\Delta t)\mathbf{a}_{i,k}\,, \qquad k = 1,2,3,\dots \tag{1.9}$$

$$\mathbf{r}_{i,k+1} = \mathbf{r}_{i,k} + (\Delta t)\mathbf{v}_{i,k+1/2}\,, \qquad k = 0,1,2,\dots\,. \tag{1.10}$$

The name "leap-frog" derives from the way position and velocity are defined at alternate, sequential time points. Note also that if (1.9) is solved for $\mathbf{a}_{i,k}$ and (1.10) is solved for $\mathbf{v}_{i,k+1/2}$, then the resulting formulae are central difference, $O((\Delta t)^2)$ approximation formulae.

If at time t_k one rewrites (1.6) and (1.7), respectively, as

$$\mathbf{F}_{i,k} = m_i\mathbf{a}_{i,k}, \qquad i = 1,2,\dots,N \tag{1.11}$$

$$\mathbf{F}_{i,k} = \mathbf{F}^{**}_{i,k} + \mathbf{F}^{*}_{i,k}, \qquad i = 1,2,\dots,N \tag{1.12}$$

then (1.8)–(1.12) determine the positions and velocities of all N particles recursively and explicitly from given initial data.

Example. To illustrate the numerical procedure to be followed, consider the following simple example in only one space dimension. On an X-axis, let P_1 and P_2, with masses $m_1 = 2, m_2 = 1$, be located initially at $x_{1,0} = 0, x_{2,0} = 1$ and have initial velocities $v_{1,0} = -1, v_{2,0} = 3$. Let the distance of local interaction be $D = 1.5$ and set $\Delta t = 0.1$. Let the forces on P_1 and P_2 at t_k be given by

$$F^{**}_{1,k} = -980\,, \tag{1.13}$$

$$F^{*}_{i,k} = \left(-\frac{1}{\left|x_{2,k} - x_{1,k}\right|^3} + \frac{2}{\left|x_{2,k} - x_{1,k}\right|^6}\right)\frac{x_{1,k} - x_{2,k}}{\left|x_{2,k} - x_{1,k}\right|}\,, \tag{1.14}$$

$$F^{**}_{2,k} = 0\,, \tag{1.15}$$

$$F^{*}_{2,k} = -F^{*}_{1,k}\,. \tag{1.16}$$

Then, from (1.8)–(1.11), one finds for P_1 that

$$v_{1,1/2} = v_{1,0} + (0.05)a_{1,0}\,, \qquad \text{(Starter formula)}$$

$$v_{1,k+1/2} = v_{1,k-1/2} + (0.1)a_{1,k}\,, \quad k = 1,2,3,\dots$$

$$x_{1,k+1} = x_{1,k} + (0.1)v_{1,k+1/2}\,, \quad k = 0,1,2,\dots$$

or, equivalently, that

$$v_{1,1/2} = -1 + (0.05)(F_{1,0}/2) = -1 + F_{1,k}(0.025)F_{1,0} \ , \tag{1.17}$$

$$v_{1,k+1/2} = v_{1,k-1/2} + (0.1)(F_{1,k}/2) = v_{1,k-1/2} + (0.05)F_{1,k} \ , \tag{1.18}$$

$$x_{1,k+1} = x_{1,k} + (0.1)v_{1,k+1/2} \ . \tag{1.19}$$

Since $|x_{2,0} - x_{1,0}| < 1.5 = D$, it follows from (1.12)–(1.14) that

$$\begin{aligned} F_{1,0} &= F^{**}_{1,0} + F^{*}_{1,0} \\ &= -980 + \left(-\frac{1}{|x_{2,0} - x_{1,0}|^3} + \frac{2}{|x_{2,0} - x_{1,0}|^6} \right) \frac{x_{1,0} - x_{2,0}}{|x_{2,0} - x_{1,0}|} \\ &= -980 + (1)(-1) = -981 \ . \end{aligned}$$

Thus, from (1.17),

$$v_{1,1/2} = -1 + (0.025)(-981) = -25.525 \ . \tag{1.20}$$

One finds in an analogus fashion that

$$\begin{aligned} v_{2,1/2} &= v_{2,0} + (0.05)a_{2,0} \ , \\ v_{2,k+1/2} &= v_{2,k-1/2} + (0.1)a_{2,k} \ , \\ x_{2,k+1} &= x_{2,k} + (0.1)v_{2,k+1/2} \ , \end{aligned}$$

and

$$v_{2,1/2} = 3 + (0.05)(F_{2,0}/1) = 3 + (0.05)F_{2,0} \ , \tag{1.21}$$

$$v_{2,k+1/2} = v_{2,k-1/2} + (0.1)(F_{2,k}/1) = v_{2,k-1/2} + (0.1)F_{2,k} \ , \tag{1.22}$$

$$x_{2,k+1} = x_{2,k} + (0.1)v_{2,k+1/2} \ . \tag{1.23}$$

Since

$$F_{2,0} = F^{**}_{2,0} + F^{*}_{2,0} \ ,$$

it follows from (1.13), (1.15) and (1.16) that

$$F_{2,0} = 0 - F^{*}_{1,0} = 1 \ .$$

Then, from (1.21),

$$v_{2,1/2} = 3.05 \ . \tag{1.24}$$

Thus, the velocities $v_{1,1/2}$ and $v_{2,1/2}$ of P_1 and P_2 at the time $t = 1/2$ have now been determined and are given by (1.20) and (1.24). The formulae (1.19) and (1.23) with $k = 0$ now yield the new positions $x_{1,1}$ and $x_{2,1}$ of P_1 and P_2, as follows:

$$x_{1,1} = x_{1,0} + (0.1)v_{1,1/2} = 0 + (0.1)(-25.525) = -2.5525 \ , \tag{1.25}$$

$$x_{2,1} = x_{2,0} + (0.1)v_{2,1/2} = 1 + (0.1)(3.05) = 1.305 \ . \tag{1.26}$$

The process now continues to determine next $v_{1,3/2}, v_{2,3/2}$. But since the distance $|x_{2,1} - x_{1,1}| = 3.8575 > 1.5 = D$, the switch is applied so that

$$F^*_{1,1} = F^*_{2,1} = 0 \ . \tag{1.27}$$

Observe also that the notation in (1.27) should always remain clear if one remembers that the *first* subscript is always the *particle number* and the *second* is always the *time step*.

Once formulae (1.17) and (1.21) have been used to determine $v_{1,1/2}$ and $v_{2,1/2}$, they are no longer used. All the remaining trajectory calculations are done with (1.18), (1.19), (1.22) and (1.23). Hence, the counter is now set to $k = 1$. From (1.18) and (1.22), then,

$$v_{1,3/2} = v_{1,1/2} + (0.05)F^{**}_{1,1} = -25.525 + (0.05)(-980) = -74.525 \ , \tag{1.28}$$

$$v_{2,3/2} = v_{2,1/2} - (0.01)F^{**}_{2,1} = 3.05 - (0.01)(0) = 3.05 \ . \tag{1.29}$$

Now, having the velocities of P_1 and P_2 at $t = 3/2$, we find their new positions from (1.19) and (1.23) to be

$$x_{1,2} = x_{1,1} + (0.1)v_{1,3/2} = -2.5525 + (0.1)(-74.525) = -10.005 \ , \tag{1.30}$$

$$x_{2,2} = x_{2,1} + (0.1)v_{2,3/2} = 1.305 + (0.1)(3.05) = 1.610 \ . \tag{1.31}$$

The counter is then increased to $k = 2$ and the iteration continues in the indicated fashion.

With regard to the leap-frog formulae and their application, several relevant observations must now be made. First, note that (1.8)–(1.12) have been given in vector form, so that they can be applied in 1, 2, or 3 space dimensions, as needed. Of course, in two dimensions, one would, in general, have

$$\begin{aligned}
\mathbf{r}_{i,k} &= (r_{i,k,x}, r_{i,k,y}) = (x_{i,k}, y_{i,k}) \\
\mathbf{v}_{i,k} &= (v_{i,k,x}, v_{i,k,y}), \\
\mathbf{a}_{i,k} &= (a_{i,k,x}, a_{i,k,y}), \\
\mathbf{F}_{i,k} &= (F_{i,k,x}, F_{i,k,y}) \ ,
\end{aligned}$$

while in three dimensions one need only append a z-component to the above formulae.

Next, note that typical FORTRAN programs for IBM, DEC, VAX, and CRAY mainframe computers are provided in the Appendices.

Finally, note that for N relatively large, that is, $N \sim 5000$, the determination of the nearest neighbor for each particle of a system will usually be the most time consuming part of any simulation. This is particularly valid in simulations of fluids. Indeed, when one simulates a solid, the near neighbors of any P_i can often be given uniquely and explicitly for all time. But when one simulates a fluid, this is not the case. For this reason, there have been a variety of "economical near-neighbor" algorithms developed recently for simulations of fluids(Boris (1986)). However, in each case, one either does not include all the neighbors or else one is forced to alter the particle ordering. In the latter case, one cannot follow the trajectory of any particular particle from an initial to a later time, and this capability is desirable for our purposes, since we may wish to explore, for example, the motion of individual particles at the onset of turbulence. Thus, we will not take advantage of "near-neighbor" algorithms, which, at present, have their primary value in molecular mechanics modelling.

Exercises

1.1 Argue for or against any one of the following:
  - (a) Mathematics is a science.
  - (b) Physics, chemistry and biology are sciences.
  - (c) Astronomy is not a science because it has no experimental component.
  - (d) All things change with time, including science.
  - (e) Astrology has aspects of science.
  - (f) Economics, sociology, and psychology are sciences.

1.2 Find the equilibrium distance for each of the following:

(a) $F = -\frac{1.2}{r^6} + \frac{1.2}{r^{12}}$.

(b) $F = -\frac{1.0}{r^6} + \frac{1.2}{r^{12}}$.

(c) $F = -\frac{1.2}{r^6} + \frac{1.0}{r^{12}}$.

1.3 Find the equilibrium distance for each of the following:

(a) $F = -\frac{1}{r^4} + \frac{1}{r^6}$.

(b) $F = -\frac{1}{r^4} + \frac{1.21}{r^6}$.

(c) $F = -\frac{1.21}{r^3} + \frac{1}{r^5}$.

1.4 Consider two particles P_1 and P_2 in motion in an XY-plane. Let P_1 have mass $m_1 = 2$ and initial data $x_{1,0} = 0, y_{1,0} = 10, v_{1,0,x} = 0, v_{1,0,y} = -15$. Let P_2 have mass $m_2 = 1$ and initial data $x_{2,0} = 10, y_{2,0} = 0, v_{2,0,x} = -10, v_{2,0,y} = -4$. Let the local distance of interaction be $D = 5$. Using the leap-frog formulae with $\Delta t = 0.01$, determine the motion of P_1 and P_2 through t_{100} for the force formulae

$$\mathbf{F}^{**}_{1,k} = (F_{1,k,x}, F_{1,k,y}) = (0, -9.8) ,$$

$$\mathbf{F}^{*}_{1,k} = \left(-\frac{1}{r^2_{12,k}} + \frac{4}{r^4_{12,k}}\right)\left(\frac{\mathbf{r}_{21,k}}{r_{12,k}}\right) ,$$

$$\mathbf{F}^{**}_{2,k} = \mathbf{F}^{**}_{1,k} , \mathbf{F}^{*}_{2,k} = -\mathbf{F}^{*}_{1,k} ,$$

$$\mathbf{r}_{ij,k} = \sqrt{(x_{i,k} - x_{j,k})^2 + (y_{i,k} - y_{i,k})^2} .$$

1.5 Repeat Exercise 1.4 but use the force formulae

$$\mathbf{F}^{**}_{1,k} = \left(-\frac{1}{r^2_{12,k}}\right)\frac{\mathbf{r}_{21,k}}{r_{12,k}} ,$$

$$\mathbf{F}^{*}_{1,k} = \left(-\frac{1}{r^3_{12,k}} + \frac{1}{r^5_{12,k}}\right)\frac{\mathbf{r}_{12,k}}{r_{12,k}} ,$$

$$\mathbf{F}^{**}_{2,k} = -\mathbf{F}^{**}_{1,k} ,$$

$$\mathbf{F}^{*}_{2,k} = -\mathbf{F}^{*}_{1,k} ,$$

$$r_{ij,k} = \sqrt{(x_{i,k} - x_{j,k})^2 + (y_{i,k} - y_{j,k})^2} \ .$$

1.6 Repeat Exercise 1.4 but use the force formulae

$$\mathbf{F}^{**}_{1,k} = \left(-\frac{1}{r^2_{12,k}}\right)\frac{\mathbf{r}_{21,k}}{r_{12,k}}, \qquad r_{12,k} > D$$

$$\mathbf{F}^{**}_{1,k} = \mathbf{0}, \qquad r_{12,k} \le D$$

$$\mathbf{F}^{*}_{1,k} = \left(-\frac{1}{r^3_{12,k}} + \frac{1}{r^5_{12,k}}\right)\frac{\mathbf{r}_{21,k}}{r_{12,k}} \ ,$$

$$\mathbf{F}^{**}_{2,k} = -\mathbf{F}^{**}_{1,k} \ ,$$

$$\mathbf{F}^{*}_{2,k} = -\mathbf{F}^{*}_{1,k} \ ,$$

$$\mathbf{r}_{ij,k} = \sqrt{(x_{i,k} - x_{j,k})^2 + (y_{i,k} - y_{j,k})^2} \ .$$

1.7 Consider two particles P_1 and P_2 in motion in three dimensions. Let P_1 have mass $m_1 = 2$ and P_2 have mass $m_2 = 1$. Let the initial data be

$$x_{1,0} = -1, y_{1,0} = 0, z_{1,0} = 0, \ \ v_{1,0,x} = 0, v_{1,0,y} = 0, v_{1,0,z} = -1 \ ,$$

$$x_{2,0} = 1, y_{2,0} = 0, z_{2,0} = 0, \ \ v_{2,0,x} = 0, v_{2,0,y} = 5, v_{2,0,z} = 1 \ .$$

Let the local distance of interaction be $D = 5$. Using the leap-frog formulae with $\Delta t = 0.01$, determine the motion of P_1 and P_2 through t_{100} for the force formulae

$$\mathbf{F}^{**}_{1,k} = (0, 0, -9.8),$$

$$\mathbf{F}^{*}_{1,k} = \left(-\frac{1}{r^2_{12,k}} + \frac{1}{r^4_{12,k}}\right)\frac{\mathbf{r}_{21,k}}{r_{12,k}} \ ,$$

$$\mathbf{F}^{**}_{2,k} = \mathbf{F}^{**}_{1,k} \ ,$$

$$\mathbf{F}^{*}_{2,k} = -\mathbf{F}^{*}_{1,k} \ ,$$

$$\mathbf{r}_{ij,k} = \sqrt{(x_{i,k} - x_{j,k})^2 + (y_{i,k} - y_{j,k})^2 + (z_{i,k} - z_{j,k})^2} \ .$$

1.8 Repeat Exercise 1.7 but use the force formulae

$$\mathbf{F}^{**}_{1,k} = \mathbf{0} \ ,$$

$$\mathbf{F}^{*}_{1,k} = \left(-\frac{1}{r^3_{12,k}} + \frac{1}{r^5_{12,k}}\right)\left(\frac{\mathbf{r}_{21,k}}{r_{12,k}}\right) \ ,$$

$$\mathbf{F}^{**}_{2,k} = \mathbf{F}^{**}_{1,k} ,$$

$$\mathbf{F}^{*}_{2,k} = -\mathbf{F}^{*}_{1,k} ,$$

$$r_{ij,k} = \sqrt{(x_{i,k}-x_{j,k})^2 + (y_{i,k}-y_{j,k})^2 + (z_{i,k}-z_{j,k})^2}$$

1.9 Repeat Exercise 1.7 but use the force formulae

$$\mathbf{F}^{**}_{1,k} = \left(-\frac{10}{r^2_{12,k}}\right)\frac{\mathbf{r}_{21,k}}{r_{12,k}}, \qquad r_{12,k} > D$$

$$\mathbf{F}^{**}_{1,k} = \mathbf{0} , \qquad r_{12,k} \le D ,$$

$$\mathbf{F}^{*}_{1,k} = \left(-\frac{1}{r^3_{12,k}} + \frac{9}{r^5_{12,k}}\right)\frac{r_{21,k}}{r_{12,k}} ,$$

$$\mathbf{F}^{**}_{2,k} = -\mathbf{F}^{**}_{1,k} ,$$

$$\mathbf{F}^{*}_{2,k} = -\mathbf{F}^{*}_{1,k} ,$$

$$r_{ij,k} = \sqrt{(x_{i,k}-x_{j,k})^2 + (y_{i,k}-y_{j,k})^2 + (z_{i,k}-z_{j,k})^2} .$$

1.10 Consider 3 particles P_1, P_2, P_3 of respective masses $m_1 = 1000$, $m_2 = 20$, $m_3 = 1$. The given initial data are

$$\begin{gathered} x_{1,0}=0,\ y_{1,0}=0,\ z_{1,0}=0,\ v_{1,0,x}=0,\ v_{1,0,y}=0,\ v_{1,0,z}=0, \\ x_{2,0}=10,\ y_{2,0}=0,\ z_{2,0}=0,\ v_{2,0,x}=0,\ v_{2,0,y}=10,\ v_{2,0,z}=0, \\ x_{3,0}=-10,\ y_{3,0}=0,\ z_{3,0}=0,\ v_{3,0,x}=0,\ v_{3,0,y}=0, \\ v_{3,0,z}=20 . \end{gathered}$$

Let no distance of local interaction be prescribed. Using the leap-frog formulae with $\Delta t = 0.01$, determine the motion from the force formulae

$$\mathbf{F}^{**}_{1,k} = \left(-\frac{m_1 m_2}{r^2_{12,k}}\right)\frac{\mathbf{r}_{21,k}}{r_{12,k}} + \left(-\frac{m_1 m_3}{r^2_{13,k}}\right)\frac{\mathbf{r}_{31,k}}{r_{13,k}} ,$$

$$\mathbf{F}^{**}_{2,k} = \left(-\frac{m_1 m_2}{r^2_{12,k}}\right)\frac{\mathbf{r}_{12,k}}{r_{12,k}} + \left(-\frac{m_2 m_3}{r^2_{23,k}}\right)\frac{\mathbf{r}_{32,k}}{r_{23,k}} ,$$

$$\mathbf{F}^{**}_{3,k} = \left(-\frac{m_1 m_3}{r^2_{13,k}}\right)\frac{\mathbf{r}_{13,k}}{r_{13,k}} + \left(-\frac{m_2 m_3}{r^2_{23,k}}\right)\frac{\mathbf{r}_{23,k}}{r_{23,k}} ,$$

$$\mathbf{F}^{*}_{1,k} = \mathbf{F}^{*}_{2,k} = \mathbf{F}^{*}_{3,k} = \mathbf{0},$$

$$r_{ij,k} = \sqrt{(x_{i,k}-x_{j,k})^2 + (y_{i,k}-y_{j,k})^2 + (z_{i,k}-z_{j,k})^2} .$$

1.11 Consider 3 particles P_1, P_2, P_3 which are in motion in the XY-plane. Assume that $m_1 = m_2 = m_3 = 1$ and that the initial data are:

$$x_{1,0} = 0.50, y_{1,0} = 0, v_{1,0,x} = -0.5, v_{1,0,y} = 0 \ ,$$
$$x_{2,0} = -0.50, y_{2,0} = 0, v_{2,0,x} = 0.5, v_{2,0,y} = 0.01 \ ,$$
$$x_{3,0} = 0, y_{3,0} = 0.87, v_{3,0,x} = 0.01, v_{3,0,y} = -0.9 \ .$$

Let all long range forces be 0 and, for $D = 2.5$, let the local force acting on P_1 at time t_k be given by

$$(1) \quad F_{1,k,x} = \left[-\frac{m_1 m_2}{r_{12,k}^3} + \frac{m_1 m_2}{r_{12,k}^5} \right] \frac{x_{1,k} - x_{2,k}}{r_{12,k}} + \left[-\frac{m_1 m_3}{r_{13,k}^3} + \frac{m_1 m_3}{r_{13,k}^5} \right] \frac{x_{1,k} - x_{3,k}}{r_{13,k}} \ ,$$

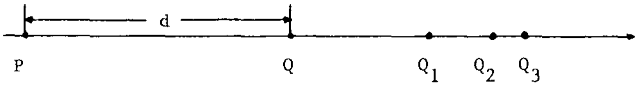
$$(2) \quad F_{1,k,y} = \left[-\frac{m_1 m_2}{r_{12,k}^3} + \frac{m_1 m_2}{r_{12,k}^5} \right] \frac{y_{1,k} - y_{2,k}}{r_{12,k}} + \left[-\frac{m_1 m_3}{r_{13,k}^3} + \frac{m_1 m_3}{r_{13,k}^5} \right] \frac{y_{1,k} - y_{3,k}}{r_{13,k}} \ ,$$

$$(3) \quad r_{ij,k} = \sqrt{(x_{i,k} - x_{j,k})^2 + (y_{i,k} - y_{j,k})^2} \ .$$

Let the local acting on P_2 be given by (1)–(2) with the numbers 1 and 2 interchanged, while that on P_3 is given by (1)–(2) with 1 and 3 interchanged. Then determine the motion of the system through $t = 2$ using the leap-frog formulae with $\Delta t = 0.0001$.

1.12 (a) Discuss the following free translation of Zeno's "Achilles and the Tortoise"" paradox.

A fast runner and a slow tortoise are to have a race. Because of the runner's superior speed, the tortoise is allowed to begin the race at a positive distance d ahead of the runner (see the figure). Let the runner's initial point be P and that of the tortoise be Q. After the race has begun, the runner must reach the point Q, which takes time, during which the tortoise moves ahead to a new point Q_1. The runner must then reach the point Q_1, which takes time, during which the tortoise moves ahead to a new point Q_2. The runner must then reach the point Q_2, which takes time, during which the tortoise moves ahead to a new point Q_3, and so forth. Thus the runner must always reach a point where the tortoise has already been, from which it follows that the runner, no matter what his speed, can never overtake the tortoise. (b) Show that if one takes a molecular viewpoint, then no paradox exists.



1.13 Show how to derive the Navier–Stokes equations from a molecular model of a fluid.

1.14 From a molecular point of view, what is fluid surface tension?