

5.2.1 Energy

The internal energy is easily obtained from a simulation as the ensemble average of the energies of the states that are examined during the course of the simulation:

$$U = \langle E \rangle = \frac{1}{M} \sum_{i=1}^M E_i$$

5.2.4 Temperature

In a canonical ensemble the total temperature is constant. In the microcanonical ensemble, however, the temperature will fluctuate. The temperature is directly related to the kinetic energy of the system as follows:

$$\mathcal{K} = \sum_{i=1}^N \frac{|\mathbf{p}_i|^2}{2m_i} = \frac{k_B T}{2} (3N - N_c) \quad (5.14)$$

In this equation, \mathbf{p}_i is the total momentum of particle i and m_i is its mass. According to the theorem of the equipartition of energy each degree of freedom contributes $k_B T/2$. If there are N particles, each with three degrees of freedom, then the kinetic energy should equal $3Nk_B T/2$. N_c in equation (5.14) is the number of constraints on the system. In a molecular dynamics simulation the total linear momentum of the system is often constrained to a value of zero, which has the effect of removing three degrees of freedom from the system and so N_c would be equal to 3. Other types of constraint are also possible discuss in section 6.5.

5.2.3 Pressure

The pressure is usually calculated in a computer simulation via the virial theorem of Clausius. The *virial* is defined as the expectation value of the sum of the products of the coordinates of the particles and the forces acting on them. This is usually written $W = \sum x_i \dot{p}_x$, where x_i is a coordinate (e.g. the x or y coordinate of an atom) and \dot{p}_x is the first derivative of the momentum along that coordinate (\dot{p}_x is the force, by Newton's second law). The virial theorem states that the virial is equal to $-3Nk_B T$.

In an ideal gas, the only forces are those due to interactions between the gas and the container and it can be shown that the virial in this case equals $-3PV$. This result can also be obtained directly from $PV = Nk_B T$.

Forces between the particles in a real gas or liquid affect the virial, and thence the pressure. The total virial for a real system equals the sum of an ideal gas part ($-3PV$) and a contribution due to interactions between the particles. The result obtained is:

$$W = -3PV + \sum_{i=1}^N \sum_{j=i+1}^N r_{ij} \frac{d\psi(r_{ij})}{dr_{ij}} = -3Nk_B T \quad (5.12)$$

The real gas part is derived in Appendix 5.3. If $d\psi(r_{ij})/dr_{ij}$ is written as f_{ij} , the force acting between atoms i and j , then we have the following expression for the pressure:

$$P = \frac{1}{V} \left[Nk_B T - \frac{1}{3k_B T} \sum_{i=1}^N \sum_{j=i+1}^N r_{ij} f_{ij} \right] \quad (5.13)$$

The forces are calculated as part of a molecular dynamics simulation, and so little additional effort is required to calculate the virial and thus the pressure. The forces are not routinely calculated during a Monte Carlo simulation, and so some additional effort is required to determine the pressure by this route. When calculating the pressure it is also important to check that the components of the pressure in all three directions are equal.

5.2.2 Heat capacity

At a phase transition the heat capacity will often show a characteristic dependence upon the temperature (a first-order phase transition is characterised by an infinite heat capacity at the transition but in a second-order phase transition the heat capacity changes discontinuously). Monitoring the heat capacity as a function of temperature may therefore enable phase transitions to be detected. Calculations of the heat capacity can also be compared with experimental results and so be used to check the energy model or the simulation protocol.

The heat capacity is formally defined as the partial derivative of the internal energy with respect to temperature:

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V \quad (5.8)$$

The heat capacity can therefore be calculated by performing a series of simulations at different temperatures, and then differentiating the energy with respect to the temperature. The differentiation can be done numerically or by fitting a polynomial to the data and then analytically differentiating the fitted function. The heat capacity may also be calculated from a single simulation by considering the instantaneous fluctuations in the energy as follows:

$$C_V = \{ \langle E^2 \rangle - \langle E \rangle^2 \} / k_B T^2 \quad (5.9)$$

An alternative way to write this expression uses the relationship

$$\langle (E - \langle E \rangle)^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2 \quad (5.10)$$

giving

$$C_V = \langle (E - \langle E \rangle)^2 \rangle / k_B T^2 \quad (5.11)$$

A derivation of this result is provided in Appendix 5.2.

The heat capacity can therefore be obtained by keeping a running count of E^2 and E during the simulation, from which their expectation values $\langle E^2 \rangle$ and $\langle E \rangle$ can be calculated at the end of the calculation. Alternatively, if the energies are stored during the simulation then the value of $\langle (E - \langle E \rangle)^2 \rangle$ can be calculated once the simulation has finished. This second approach may be more accurate due to round-off errors; $\langle E^2 \rangle$ and $\langle E \rangle^2$ are usually both large numbers and so there may be a large uncertainty in their difference.

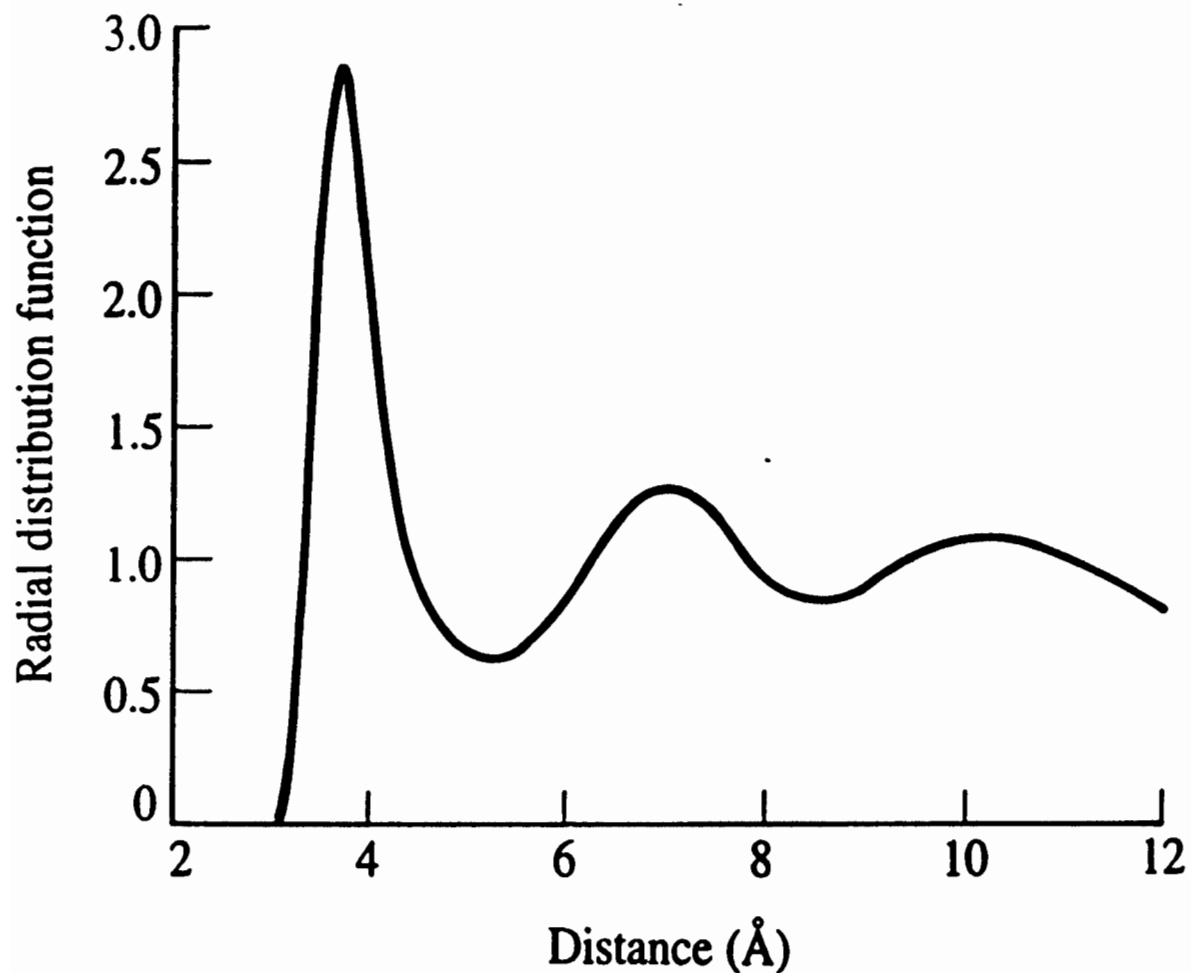
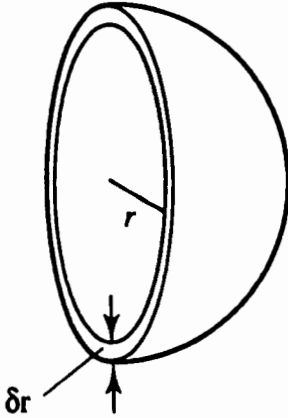


Fig. 5.2 Radial distribution function determined from a 100 ps molecular dynamics simulation of liquid argon at a temperature of 100 K and a density of 1.396 g cm^{-3} .

5.2.5 Radial distribution functions

To calculate the pair distribution function from a simulation, the neighbours around each atom or molecule are sorted into distance 'bins', or histograms. The number of neighbours in each bin is then averaged over the entire simulation. For



example, a count is made of the number of neighbours between (say) 2.5 Å and 2.75 Å, 2.75 Å and 3.0 Å and so on for every atom or molecule in the simulation. This count can be performed during the simulation itself or by analysing the configurations that are generated.

Thermodynamic properties can be calculated using the radial distribution function, if pairwise additivity of the forces is assumed. These properties are usually given as an ideal gas part plus a real gas part. For example, to calculate the energy of a real gas, we consider the spherical shell of volume $4\pi r^2 \delta r$ that contains $4\pi r^2 \rho g(r) \delta r$ particles. If the pair potential at a distance r has a value $\psi(r)$ then the energy of interaction between the particles in the shell and the central particle is $4\pi r^2 \rho g(r) \psi(r) \delta r$. The total potential energy of the real gas is obtained by integrating this between 0 and ∞ and multiplying the result by $N/2$ (the factor 1/2 ensures that we only count each interaction once). The total energy is then given by:

$$E = \frac{3}{2} N k_B T + 2\pi N \rho \int_0^{\infty} r^2 \psi(r) g(r) dr \quad (5.16)$$

In a similar way the following expression for the pressure can be derived:

$$PV = N k_B T - \frac{2\pi N \rho}{3 k_B T} \int_0^{\infty} r^2 r \frac{d\psi(r)}{dr} g(r) dr \quad (5.17)$$

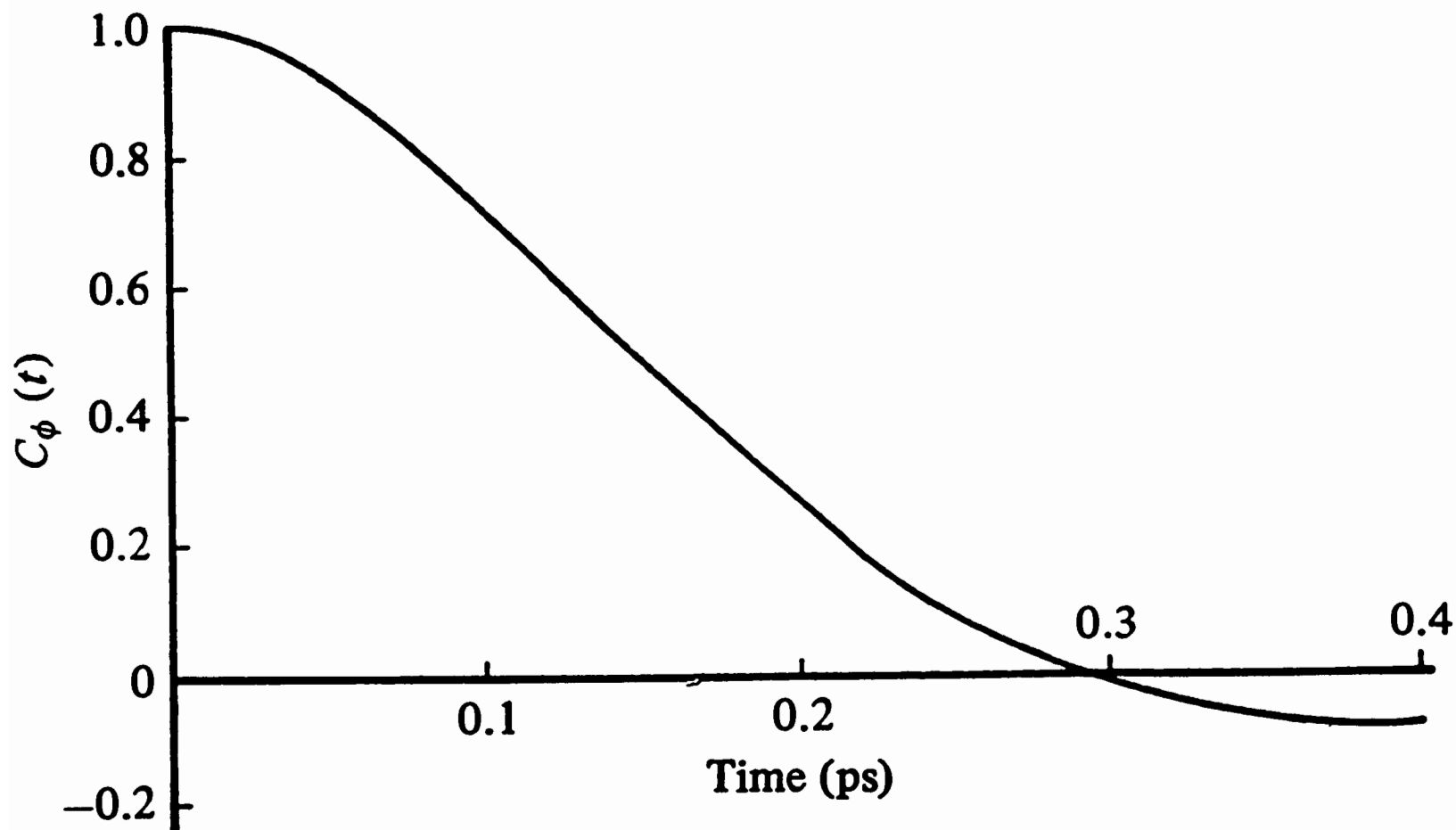


Fig. 5.6. The normalized time correlation function, $C_\phi(t) = \langle \Delta\phi(t) \Delta\phi(0) \rangle / \langle \Delta\phi(0) \Delta\phi(0) \rangle$, for torsional fluctuations $\Delta\phi$ of the tyrosine 21 ring in a molecular dynamics simulation of the pancreatic trypsin inhibitor (McCammon *et al.*, 1979).

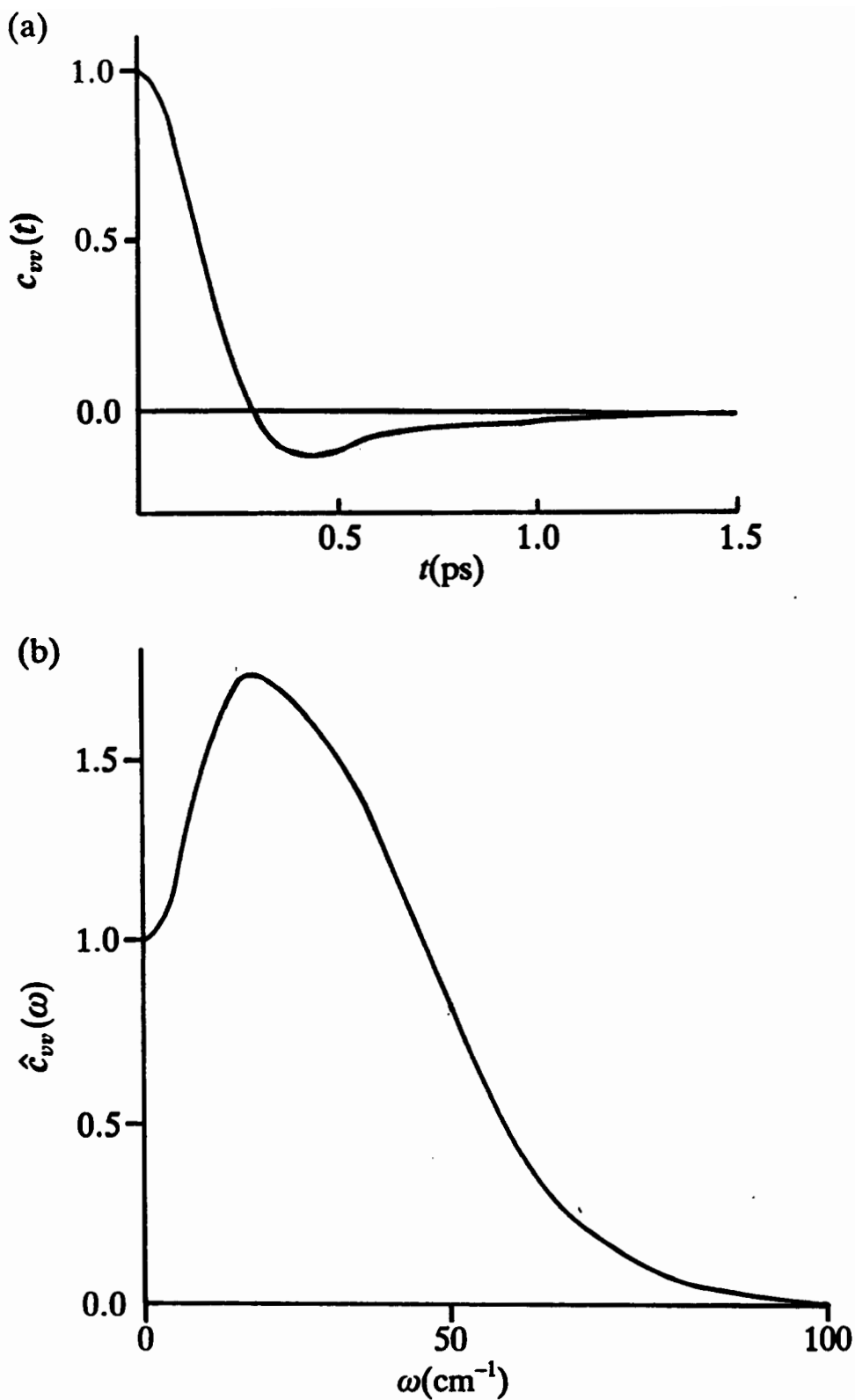


Fig. 2.3 (a) The velocity autocorrelation function and (b) its Fourier transform, for the Lennard-Jones liquid near the triple point ($\rho^* = 0.85$, $T^* = 0.76$).

The temporal Fourier transform (see Appendix D) of the velocity autocorrelation function is proportional to the density of normal modes in a purely harmonic system, and is often loosely referred to as the 'density of states' in solids and liquids.

We shall consider the formulae for two properties in detail because these will be calculated in the example program of the next section. The first property is the diffusion coefficient for a species i , D_i , which is proportional to the time integral of its velocity autocorrelation function:

$$D_i = \frac{1}{3} \int_0^{\infty} dt \langle v_i^T(t) v_i(0) \rangle \quad (10.8)$$

This equation can be integrated by parts to give the following expression which is valid at long times, t :

$$6tD_i = \langle (r_i(t) - r_i(0))^2 \rangle \quad (10.9)$$

Equation (10.9) is an example of an *Einstein relation* for a transport coefficient. The average on the right-hand side of equation (10.9) is closely related to that of a time correlation function and it can be calculated in a very similar fashion. The only difference is that, instead of taking the average of the product of the property at two different times as in equation (10.7), the averaging is performed over the square of the difference of the property at the two times.

Plots of the simulation results are shown in figures 10.1 and 10.2. The value of the diffusion coefficient can be calculated from the slope of the line in figure 10.1 at large times, giving a value of $0.42 \text{ \AA}^2 \text{ ps}^{-1}$ or $4.2 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, which is large relative to the experimental value of $2.3 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ at $25 \text{ }^\circ\text{C}$. To verify this result fully, a similar analysis would have to be carried out on a longer trajectory to ensure that the function plotted in figure 10.1 had indeed reached its limiting value at long times.

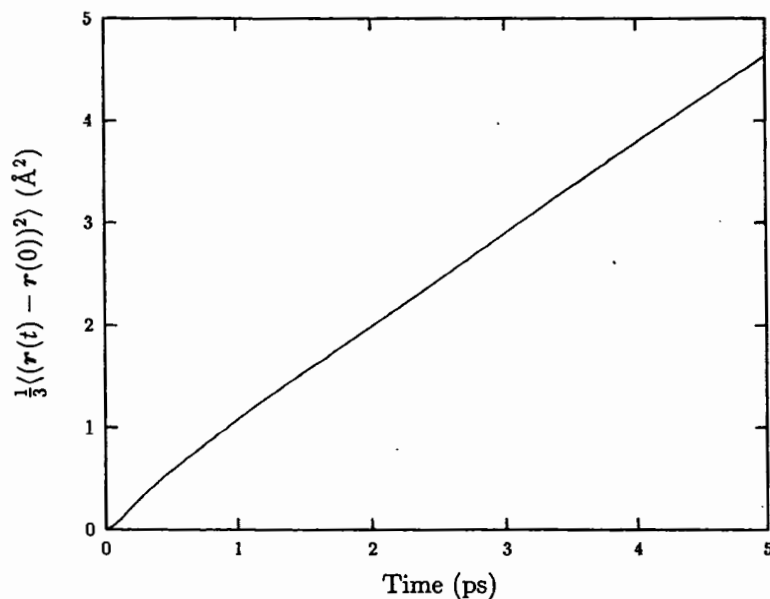
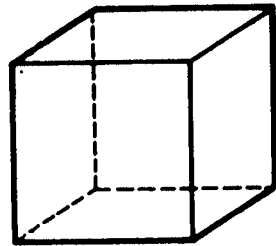
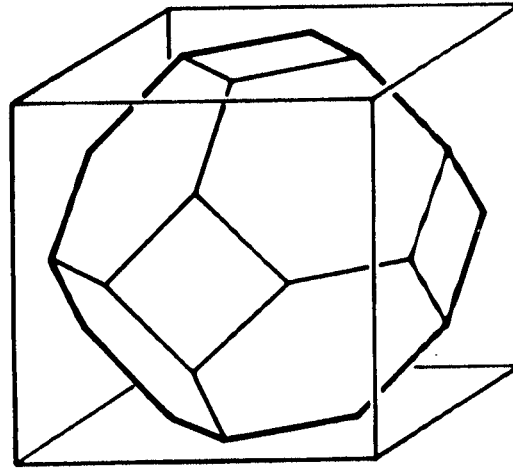


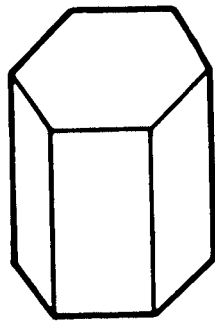
Figure 10.1. The function $\frac{1}{3} \langle (r(t) - r(0))^2 \rangle$ calculated for the oxygen atoms of the water molecules using the molecular dynamics trajectory generated in Example 16.



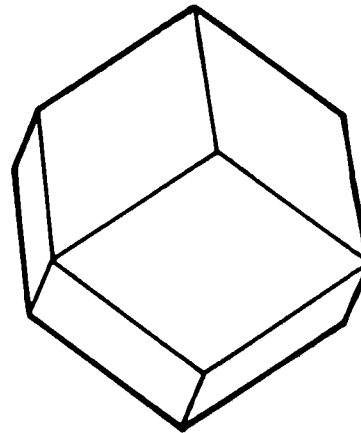
Cube



Truncated octahedron



Hexagonal prism



Rhombic dodecahedron

Fig. 5.5 Periodic cells used in computer simulations: the cube, parallelepiped, truncated octahedron, hexagonal prism and rhombic dodecahedron.

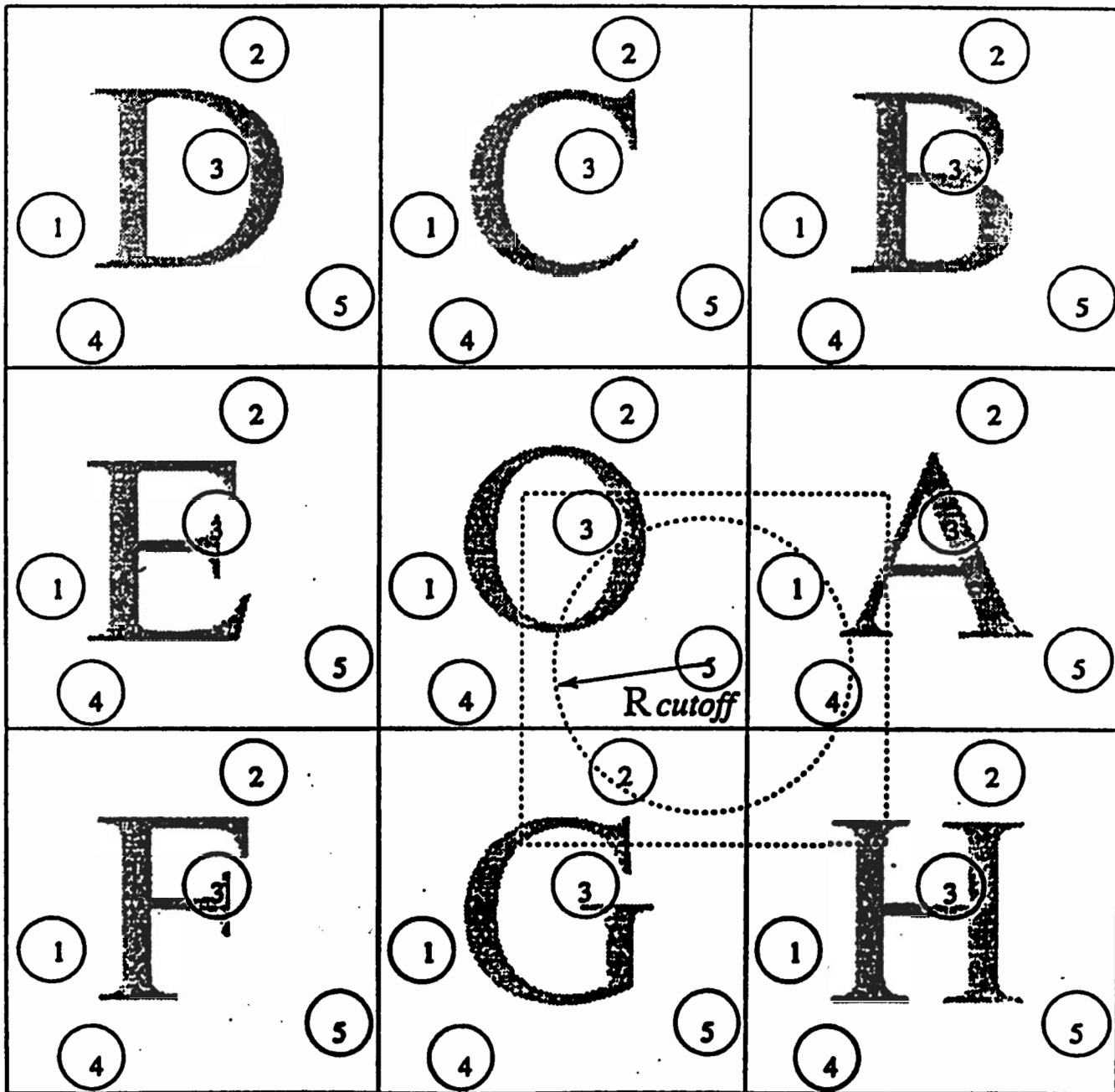
Point Charges

Let us first consider a system consisting of positively and negatively charged particles. These particles are assumed to be located in a cube with diameter L (and volume $V = L^3$). We assume periodic boundary conditions. The total number of particles in the fundamental simulation box (the unit cell) is N . We assume that at short distances the particles repel one another. In addition we assume that the system as a whole is electrically neutral; that is, $\sum_i z_i = 0$. We wish to compute the Coulomb contribution to the potential energy of this system,

$$\mathcal{U}_{\text{Coul}} = \frac{1}{2} \sum_{i=1}^N z_i \phi(\mathbf{r}_i), \quad (\text{B.1.1})$$

where $\phi(\mathbf{r}_i)$ is the electrostatic potential at the position of ion i :

$$\phi(\mathbf{r}_i) = \sum_{j,n}' \frac{z_j}{|\mathbf{r}_{ij} + \mathbf{n}L|}, \quad (\text{B.1.2})$$



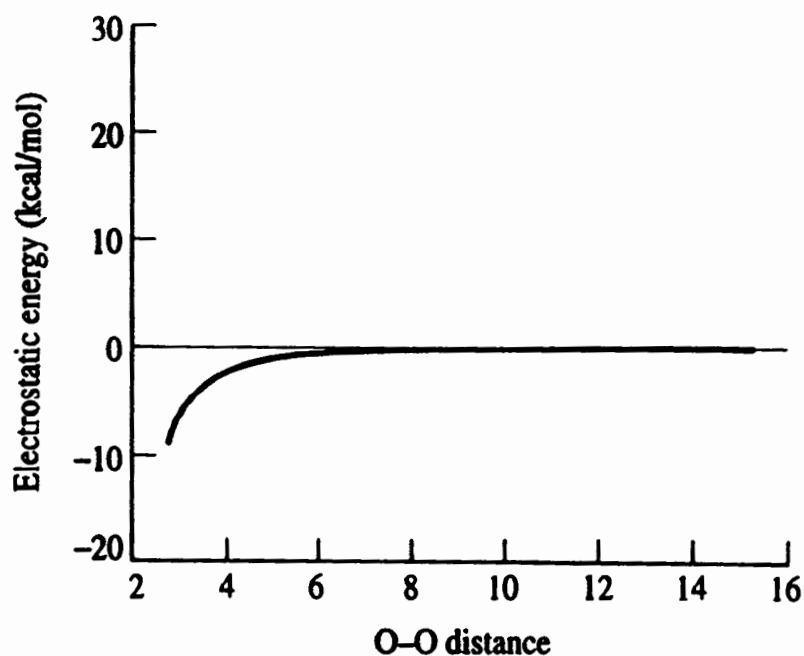


Fig. 5.13 The variation in the electrostatic interaction energy of the water dimer as a function of the O-O distance without a cutoff.

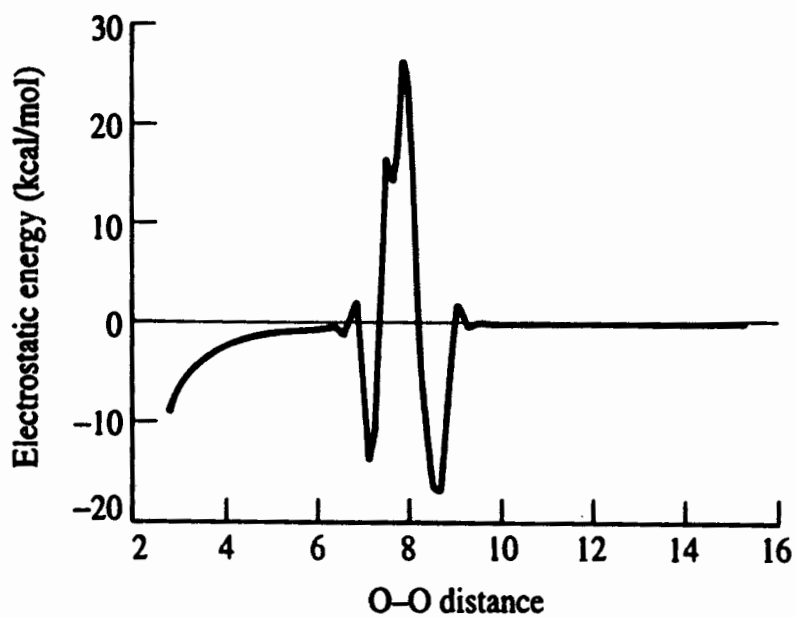


Fig. 5.14 The variation in interaction of the water dimer as a function of the O-O distance with an 8 Å atom-based cutoff.

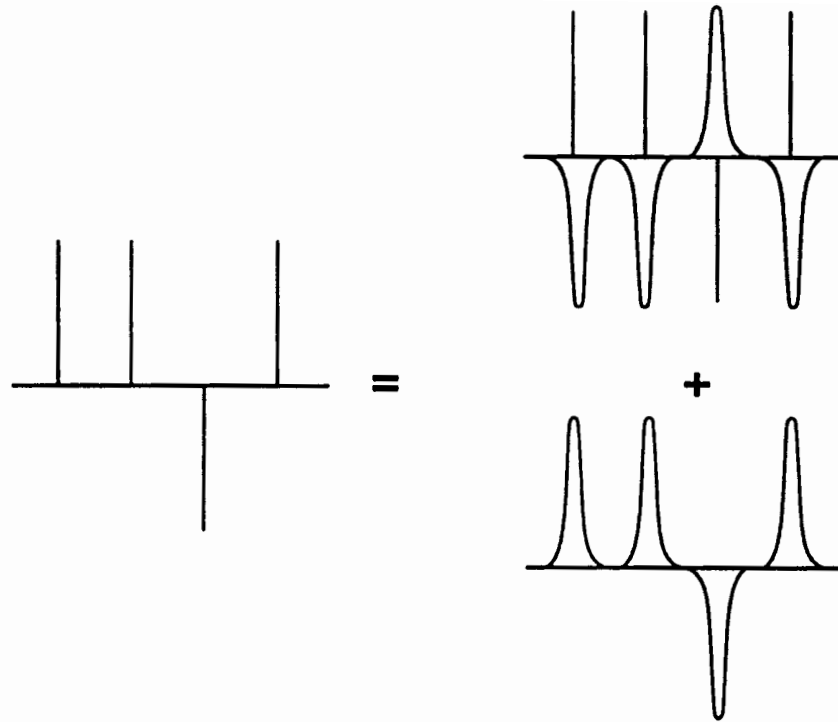


Figure B.1: A set of point charges may be considered a set of screened charges minus the smoothly varying screening background.

After this brief sketch of the method to evaluate the electrostatic contribution to the potential energy, let us now consider the individual terms. We assume that the compensating charge distribution surrounding an ion i is a Gaussian with width $\sqrt{2/\alpha}$:

$$\rho_{\text{Gauss}}(r) = -z_i(\alpha/\pi)^{\frac{3}{2}} \exp(-\alpha r^2),$$

where the choice of α is determined later by considerations of computational efficiency. We shall first evaluate the contribution to the Coulomb energy due to the continuous background charge, then compute the spurious “self” term, and finally the real-space contribution due to the screened charges.

Real-Space Sum

Finally, we must compute the electrostatic energy due to the point charges screened by oppositely charged Gaussians. Using the results of section B.1, in particular equation (B.1.10), we can immediately write the (short range) electrostatic potential due to a point charge z_i surrounded by a Gaussian with net charge $-z_i$:

$$\begin{aligned}\phi_{\text{short range}}(r) &= \frac{z_i}{r} - \frac{z_i}{r} \operatorname{erf}(\sqrt{\alpha}r) \\ &= \frac{z_i}{r} \operatorname{erfc}(\sqrt{\alpha}r),\end{aligned}\quad (\text{B.1.12})$$

where the last line defines the complementary error function $\operatorname{erfc}(x) \equiv 1 - \operatorname{erf}(x)$. The total contribution of the screened Coulomb interactions to the potential energy is then given by

$$U_{\text{short range}} = \frac{1}{2} \sum_{i \neq j}^N z_i z_j \operatorname{erfc}(\sqrt{\alpha}r_{ij}) / r_{ij}. \quad (\text{B.1.13})$$

The total electrostatic contribution to the potential energy now becomes the sum of equations (B.1.6), (B.1.11), and (B.1.13):

$$\begin{aligned}U_{\text{Coul}} &= \frac{1}{2} \sum_{\mathbf{k} \neq 0} \frac{4\pi V}{k^2} |\rho(\mathbf{k})|^2 \exp(-k^2/4\alpha) \\ &\quad - (\alpha/\pi)^{\frac{1}{2}} \sum_{i=1}^N z_i^2 \\ &\quad + \frac{1}{2} \sum_{i \neq j}^N z_i z_j \operatorname{erfc}(\sqrt{\alpha}r_{ij}) / r_{ij}.\end{aligned}\quad (\text{B.1.14})$$

Fourier Part

We must compute the electrostatic potential at a point \mathbf{r}_i due to a charge distribution $\rho_1(\mathbf{r})$ that consists of a periodic sum of Gaussians:

$$\rho_1(\mathbf{r}) = \sum_{j=1}^N \sum_{\mathbf{n}} z_j (\alpha/\pi)^{\frac{3}{2}} \exp \left[-\alpha |\mathbf{r} - (\mathbf{r}_j + \mathbf{n}L)|^2 \right].$$

To compute the electrostatic potential $\phi_1(\mathbf{r})$ due to this charge distribution, we use Poisson's equation:

$$-\nabla^2 \phi_1(\mathbf{r}) = 4\pi \rho_1(\mathbf{r}),$$

or in Fourier form,

$$\mathbf{k}^2 \phi_1(\mathbf{k}) = 4\pi \rho_1(\mathbf{k}).$$

$$\begin{aligned} \mathcal{U}_1 &\equiv \frac{1}{2} \sum_i z_i \phi_1(\mathbf{r}_i) \\ &= \frac{1}{2} \sum_{\mathbf{k} \neq 0} \sum_{i,j=1}^N \frac{4\pi z_i z_j}{V k^2} \exp[i\mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r}_j)] \exp(-k^2/4\alpha) \\ &= \frac{V}{2} \sum_{\mathbf{k} \neq 0} \frac{4\pi}{k^2} |\rho(\mathbf{k})|^2 \exp(-k^2/4\alpha), \end{aligned}$$

where we have used the definition

$$\rho(\mathbf{k}) \equiv \frac{1}{V} \sum_{i=1}^N z_i \exp(i\mathbf{k} \cdot \mathbf{r}_i).$$

Correction for Self-Interaction

The contribution to the potential energy given in equation (B.1.6) includes a term $(1/2)z_i \phi_{\text{self}}(\mathbf{r}_i)$ due to the interaction between a continuous Gaussian charge cloud of charge z_i and a point charge z_i located at the center of the Gaussian. This term is spurious, and we should correct for it. We therefore must compute the potential energy at the origin of a Gaussian charge cloud. The charge distribution that we have overcounted is

$$\rho_{\text{Gauss}}(\mathbf{r}) = z_i (\alpha/\pi)^{\frac{3}{2}} \exp(-\alpha r^2).$$

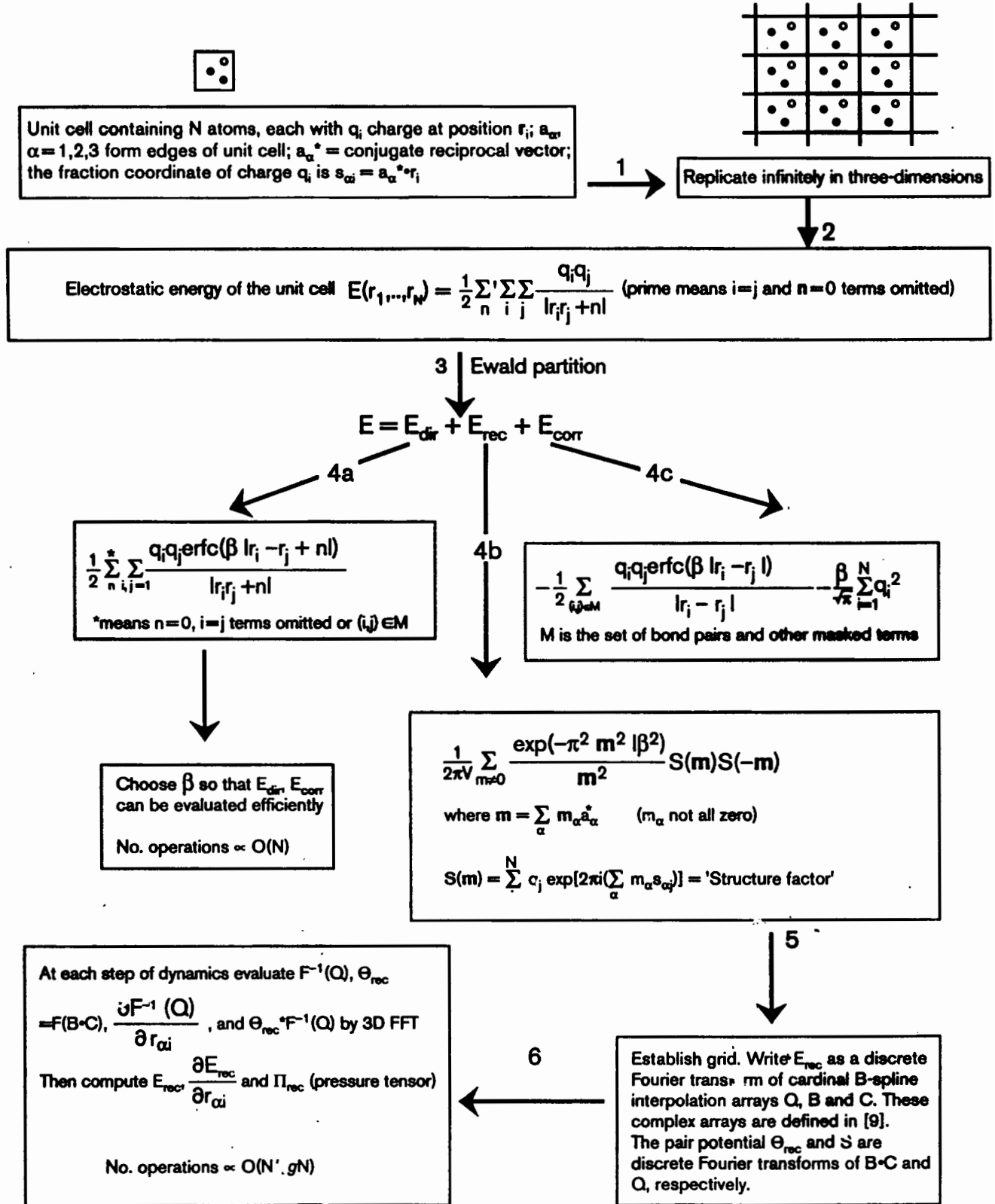
To compute the spurious self term to the potential energy, we must compute $\phi_{\text{Gauss}}(\mathbf{r})$ at $\mathbf{r} = 0$. It is easy to verify that

$$\phi_{\text{Gauss}}(\mathbf{r} = 0) = 2z_i (\alpha/\pi)^{\frac{1}{2}}.$$

Hence, the spurious contribution to the potential energy is

$$\begin{aligned} \mathcal{U}_{\text{self}} &= \frac{1}{2} \sum_{i=1}^N z_i \phi_{\text{self}}(\mathbf{r}_i) \\ &= (\alpha/\pi)^{\frac{1}{2}} \sum_{i=1}^N z_i^2. \end{aligned}$$

A flow chart of the steps involved in computing the electrostatic energy, force and pressure tensor by the PME scheme [9]. E_{dir} , E_{rec} and E_{corr} denote the direct and reciprocal summations, and the correction terms.



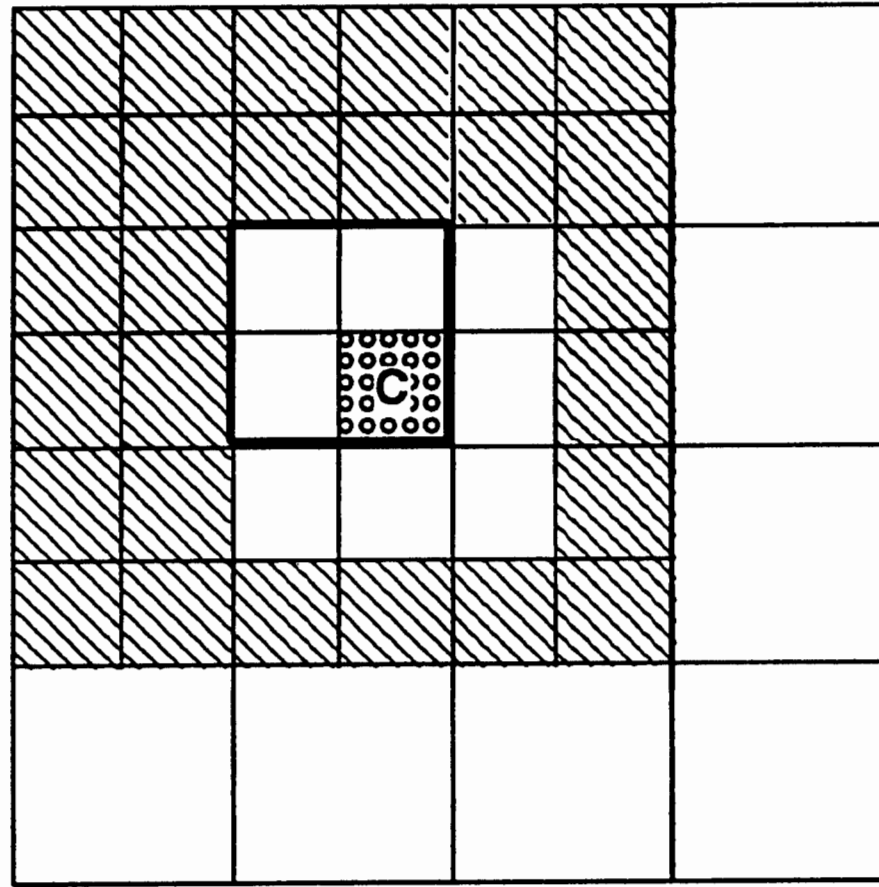


Figure B.4: The same level cells (shaded) of which the multipole potentials are transferred to the current cell to give the local expansion. The current cell is denoted by C, the neighbors of C do not contribute because they touch C. The white cells of the parent level did not touch the parent cell of C (indicated with a thick line) and therefore did contribute to the local expansion of the parent cell.

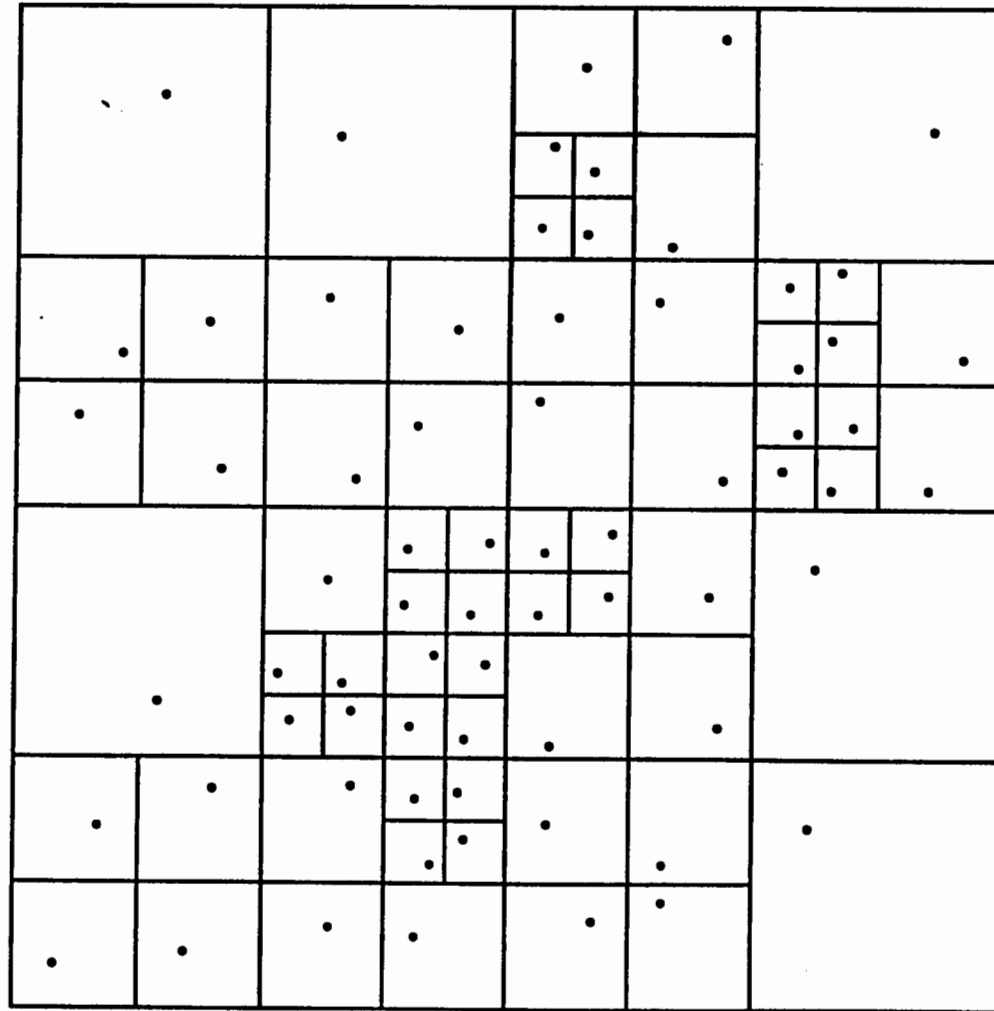


Figure 1.2: Two-dimensional representation of the Barnes-Hut adaptive oct-tree spatial decomposition. In this case, subdivision into squares, rather than cubes, continues down the quad-tree until each cell (square) contains only one particle.

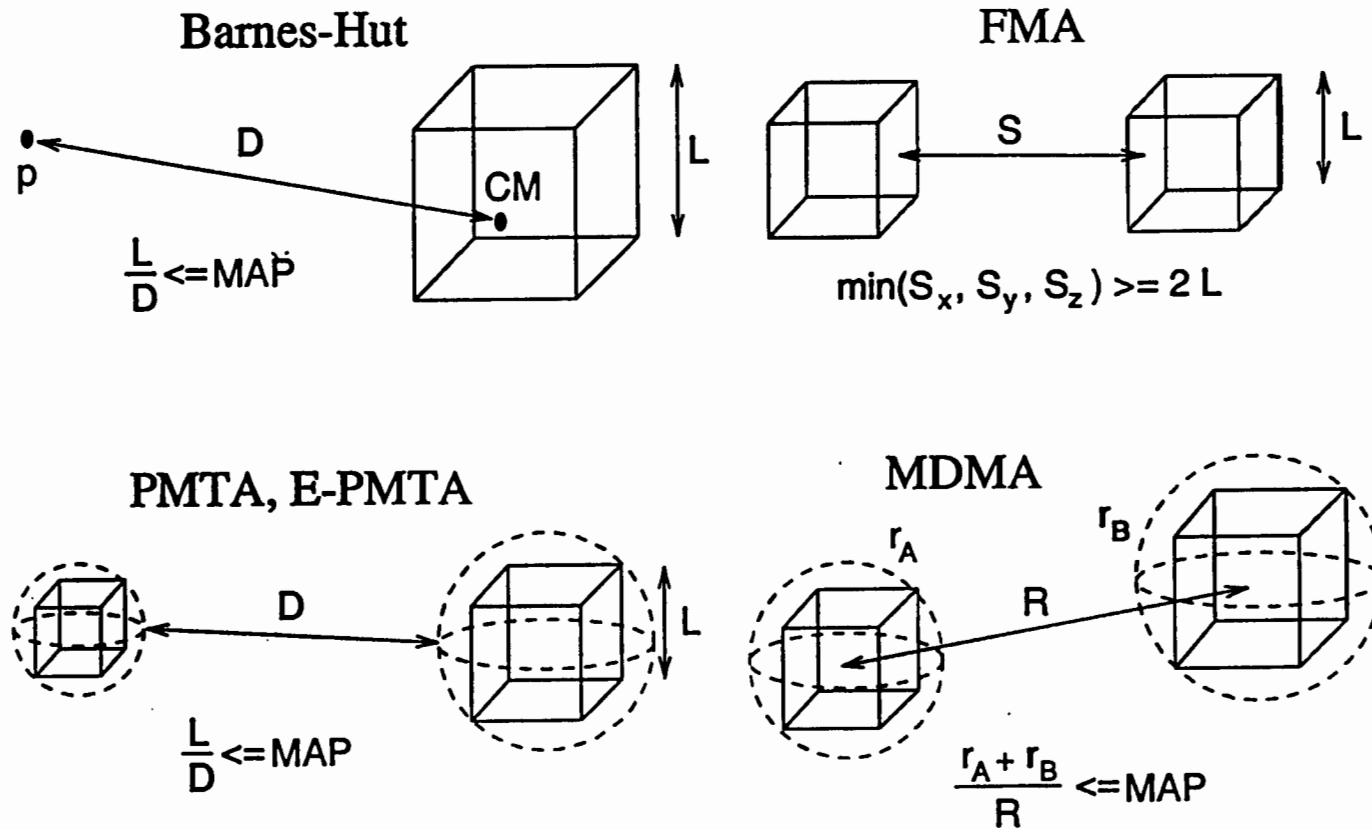


Figure 1.3: A comparison of the well-separatedness criteria for several algorithms. Multipole Acceptance Parameter (MAP) is a number used to determine whether an interaction is well-separated enough to occur based on the contribution to error. If the interaction fails for a given MAP, the participating particles must interact further down the tree. Except for the FMA, the MAP is a number such that $0 < \text{MAP} < 1$. For the Barnes-Hut tree code, the criterion is based on the separation of a particle and the center of mass of a cell. All other criteria shown are based on cell-cell separations and depend on the cell geometries rather than the location of particles in the cells.