COMPUTER SIMULATION STUDIES OF THE LIQUID STATE *

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Computer programmes have been developed for the simulation of atomic motion in liquids using the molecular dynamics method. The aims of this work are to study the relationship between the interparticle potential and liquid state properties and to produce data for the testing of theoretical models.

Recent work has concentrated on increasing the number of particles to a few thousand and increasing the time step, in order to investigate the 'hydrodynamic limit'.

1. Introduction

For a number of years now computer simulation studies of liquids have been having an increasing impact on our understanding of the liquid state. In this paper, a number of applications of the molecular dynamics method are reviewed. The general method of molecular dynamics for liquids is now well known. However, in section 2, we draw attention to some of the features of the molecular dynamics programmes in use at Harwell, which are felt to be advantageous.

The remainder of the paper is devoted to a discussion of some of the applications of the method. These are (a) investigations of the relative importance of the attractive part of the Lennard-Jones potential (b) the velocity autocorrelation function and diffusion constant for the Lennard-Jones and inverse twelfth power potentials and (c) a test of the 'self-consistent' theory of the Hutchinson and Conkie [1] for the predictions of equation of state and pair distribution functions for inverse power potentials.

2. Computational methods

The molecular dynamics method involves the solution of the classical equations of motion of a system of particles enclosed in a box, interacting

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with a potential function $\Phi(\{r_i\})$ of the coordinates of the particles. In order to avoid surface effects (in the study of equilibrium properties) and to give equal weight to all particles, periodic boundary conditions are imposed. This means that in calculating correlation functions one is strictly restricted to wavelengths commensurate with the box. Thus to investigate phenomena in the thermodynamic limit it is desirable to increase the number, N, of particles as much as possible.

Provided that the time for computation of one time step can be made to increase proportionately to N, there are other advantages to be gained even in the range of wavelength comparable to the atomic spacing. For static properties, the number of configurations required to obtain say, the pair distribution function, is proportional to N^{-1}, so that the total computation time is independent of N, while starting from a disordered array with a large number of particles gives the possibility of a greater variety of configurations than the relatively slow evolution of configurations obtained by the time development of a smaller number of particles.

For potentials of finite range, a method has been used in which the time step is proportional to N. This involves sorting the particles at *each* time step into cells, and only calculating distances between particles in cells which are within the interaction range. It turns out that the computation time is sensitive to the size of cell, the optimum being achieved with an average of about four particles per cell.

Other points of interest, in which our methods differ from molecular dynamics methods described in the literature [2, 3], are as follows.

(i) The runs are initiated by placing the particles on a face-centred cubic lattice and giving them random displacements (rather than random velocities). In this way a greater degree of spatial disorder may be introduced initially. Since a velocity distribution approximating the equilibrium distribution is acquired very rapidly in this way (after ten to twenty time steps), there is no loss in starting the particles from rest. The initial energy is then set by the maximum displacement allowed in generating the initial configuration. The energy is then adjusted by scaling the velocities until the required temperature is obtained.

(ii) The algorithm used to increase the time step is given by

$$r(t + \Delta t) = r(t) + v(t) \Delta t$$
$$+ \tfrac{1}{6} [4a(t) - a(t - \Delta t)] \Delta t^2 ,$$
$$v(t + \Delta t) = v(t)$$
$$+ \tfrac{1}{6} [2a(t + \Delta t) + 5a(t) - a(t - \Delta t)] \Delta t ,$$

where $r(t)$, $v(t)$ and $a(t)$ are the position, velocity and acceleration of a particle at time t. This algorithm, introduced by Beeman, is very strongly conserving and allows a long time step to be used. Typically one may use Δt such that $\omega_E \Delta t \approx 0.3$ where ω_E is the Einstein frequency defined by $(\langle a^2\rangle/\langle v^2\rangle)^{\frac{1}{2}}$. In such a case one may find fluctuations in energy per particle of the order of 0.5% of kT, but no tendency for the energy to vary by more than this from its mean value over several thousand time steps.

(iii) One problem with the molecular dynamics method is to know when a run has settled down to give a true uniform steady state distribution, since with a few hundred particles there will be fluctuations in the kinetic temperature of the order of 10%. One criterion used in our calculations is to keep a record of the momentum transmitted across the boundaries of the box (the external kinetic pressure, p_K) and the stress exerted across the boundaries (giving the external configurational pressure p_c). When these are equal to the internal pressures evaluated from the virial expression, it is assumed that sufficient time steps have been taken at least to give accurate ensemble averages for static properties.

3. Applications

3.1. Effect of attractive part of Lennard-Jones potential

A series of runs have been performed to examine the effect of the attractive part of the Lennard-Jones potential.

$$\phi_{LJ}(R) = 4\epsilon\left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^6\right] .$$

The computations were performed taking

$$\phi(R) = \phi_{LJ}(R) - \phi_{LJ}(R_o) \qquad R < R_o ,$$
$$= 0 \qquad\qquad\qquad R < R_o ,$$

for two values of (R_o/σ): (i) $2^{\frac{1}{6}}$ and (ii) 2.25.

(i) corresponds to taking the repulsive part alone while (ii) contains most of the attraction. The calculations were done at three state points (n, T) as shown in table 1. Figs. 1–3 show some results for a point near the Lennard-Jones triple point.

Fig. 1 shows the first peak in the pair distribution function $g(R)$. Figs. 2 and 3 show respectively the mean square displacement of an atom as a function of time, and the normalised velocity autocorrelation function $\langle v(0) \cdot v(t)\rangle/\langle v^2\rangle$.

The results for the pair distribution function have been fitted with some success by Gubbins et al. [4], using a perturbation theory in which the repulsive potential is treated as a perturbation around the hard sphere value, and the attractive contribution is calculated in first order, in a manner similar to the theory of Weeks et al.[5].

The results for the mean square displacement and the self-diffusion have not been analysed theoretically. An interesting point is that at short times the curves are very similar, indicating that the motion of atoms at short times is dominated by the repulsion of neighbouring atoms, the retarding effect of the attraction only playing a role at later times. Our values for the diffusion coefficient are in good agreement with those of Levesque and Verlet [6].

3.2. Diffusion constants for the inverse 12th power potential [7]

The properties of particles interacting with inverse

Table 1.

Molecular dynamics results for Lennard-Jones potential cut-off at R_0. The absolute values quoted are appropriate for argon (ϵ = 119.8 $^\circ$K, σ = 3.40 Å). (a) p is the pressure calculated with the cutoff potential; p_f is the pressure calculated with the full L.J. potential with the $g(R)$ calculated by molecular dynamics. ω_E is the Einstein frequency for argon calculated in the same way. (b) The figures in parentheses are those of Levesque and Verlet [6] for neighbouring state points. The discrepancy is within the 5% accuracy claimed for the calculations

(a) Static properties

n (A^{-3})	T ($^\circ$K)	$n\sigma^3$	kT/ϵ	R_0/σ	p/nkT	p_f/nkT	$\omega_E \times 10^{-13}$ (sec^{-1})
1.438	87.4	0.845	0.729	2.2500	1.92	0.22	0.77
1.438	87.2	0.845	0.728	1.1225	10.45	1.54	0.81
1.347	95.2	0.791	0.795	2.2500	1.29	−0.16	0.72
1.347	95.2	0.791	0.795	1.1225	8.60	0.72	0.75
1.065	131.1	0.626	1.095	2.2500	0.77	−0.06	0.62
1.065	130.3	0.626	1.088	1.2225	4.86	0.06	0.62

(b) Diffusion coefficients

n (A^{-3})	T ($^\circ$K)	$\tilde{n}$	R_0/σ	$D \times 10^7$ (m/sec)	D_{md}
1.438	87.4	0.914	2.2500	1.64	0.0051 (0.0048)
1.438	87.2	0.914	1.1225	2.20	0.0068
1.347	95.2	0.838	2.2500	2.91	0.0087 (0.0082)
1.347	95.2	0.838	1.1225	3.25	0.0097
1.065	131.1	0.612	2.2500	8.20	0.0213 (0.0226)
1.065	130.3	0.613	1.1225	8.33	0.0217

power law potentials of the form $\phi_\nu (R) = 4\epsilon(\sigma/R)^\nu$ are an interesting field of study since the configuration properties depend on temperature and density through a parameter $\tilde{n}$ given by

$$\tilde{n} = n\sigma^3 (\epsilon/kT)^{3/\nu} .$$

In particular, for $\nu = 12$, this potential gives the high temperature limit of the Lennard-Jones potential.

We have calculated the mean square displacement and velocity autocorrelation function for various values of $\tilde{n}$ for this value of ν. The diffusion coefficient may be written in terms of a dimensionless function $D_{md} (\tilde{n})$ as

$$D = (48)^{\frac{1}{2}} (kT/M)^{\frac{1}{2}} \sigma(\epsilon/kT)^{\frac{1}{12}} D_{md} .$$

The results are shown in fig. 4 which also show the results for the Lennard-Jones potential for $\epsilon/kT = 1$, and for the repulsive part of this potential for the three state points of table 1.

Ross and Schofield [6] have shown how the results for D_{md} may be fitted with a rigid sphere model in which the sphere radius is chosen by a free energy minimisation procedure.

3.3. Equation of state and pair distribution function for repulsive potentials

Hutchinson and Conkie [1] have recently proposed a self-consistent method for calculating the pair distribution function for repulsive potentials. In their theory, the pair distribution function, $g(R)$, the direct correlation function $c(R)$ and the potential are related by

$$g(R) - c(R) - 1 = (1/s)(\{g(R) \exp [\phi(R)/kT]\}^s -1),$$

where the parameter s is chosen so that the pressure and compressibility equations give rise to the same isotherms.
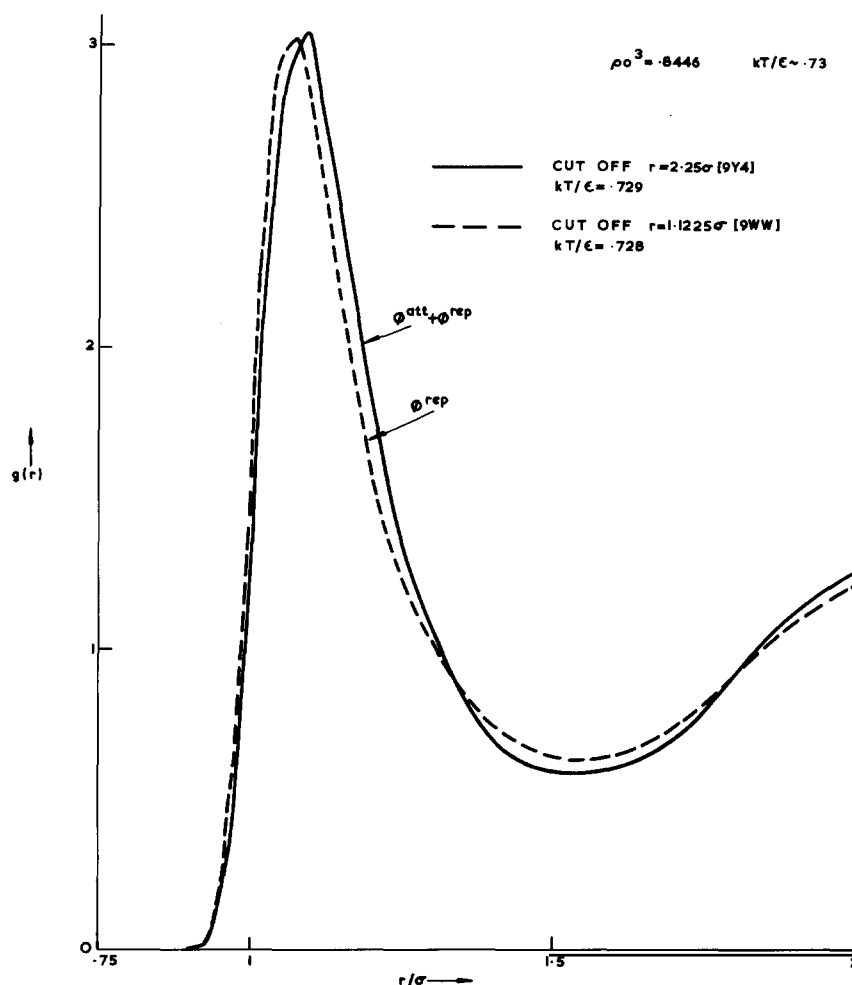
Fig. 1. Pair distribution function for Lennard-Jones potential cutoff at $r = 2.25\ \sigma$ and $r = 1.1225\sigma$.

For the inverse power potentials with $\nu = 6$ and 12 the isotherms are in good agreement with the Monte Carlo results of Hoover et al. [8]. The pair distribution functions at a density near the phase transition point are shown in figs. 5 and 6, where a comparison with Percus–Yevick theory and molecular dynamics calculations are given. The self-consistent theory is in excellent agreement with the latter, while the Percus–Yevick theory is clearly unsatisfactory at these densities.

4. Discussion

The calculations summarized here are examples of the way in which the molecular dynamics method may be used to investigate the relation between liquid state properties and the interatomic potentials, as well as providing data for the assessment of theoretical calculations.

In addition to the work reported here, similar investigations of a number of other topics are
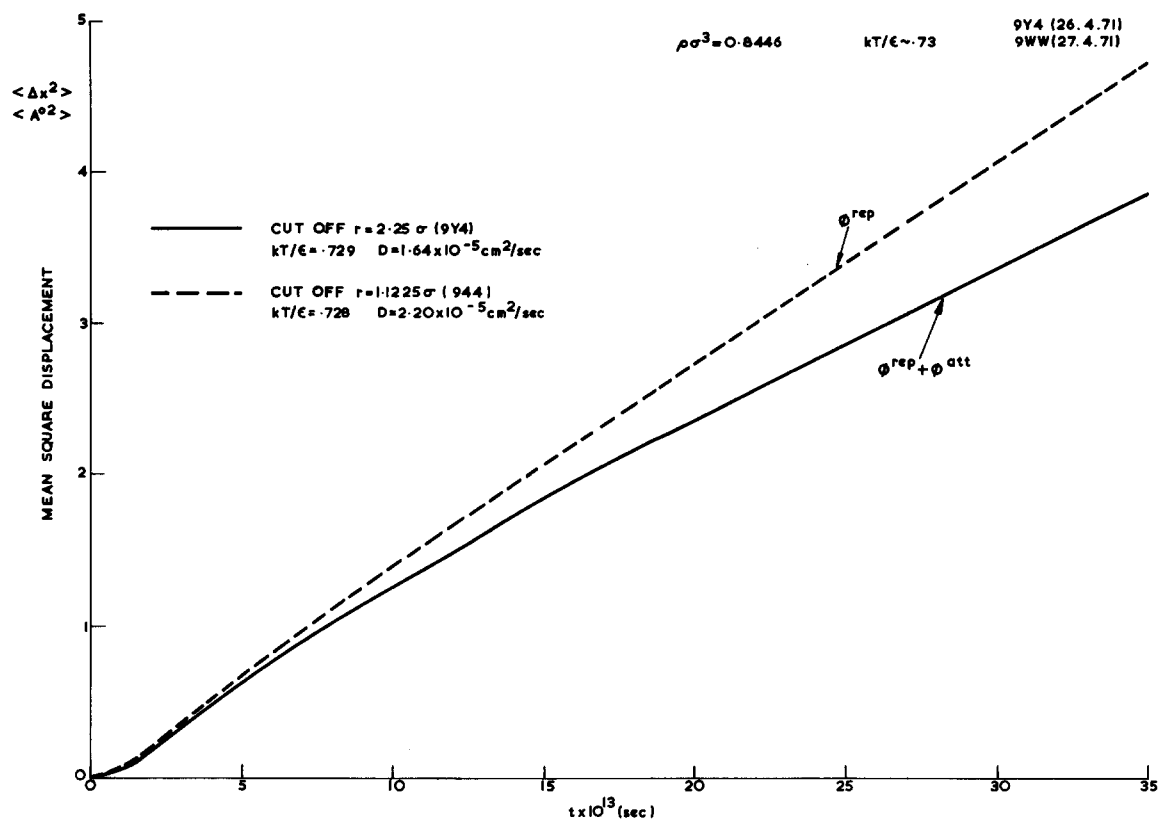
Fig. 2. Mean square displacement a particle in the two potentials of fig. 1.

currently being undertaken. These include the following. (a) A study of the so-called 'inverse problem' of obtaining information about interatomic forces from the pair distribution (or its Fourier transform, the structure factor), using the self-consistent theory mentioned above. (b) An investigation of the hard core problem, by analysing the stress—stress correlation functions. This is needed in order to understand an apparent contradiction between theories of the dynamical structure factor, $S(\kappa,\omega)$, which depend heavily on the fourth frequency moment and the ability to predict many properties using a rigid sphere model for which the fourth moment is infinite. (c)

To try exploit the ability to do calculation with up to 4000 particles in the calculation of transport coefficients, and in the study of phase boundaries.
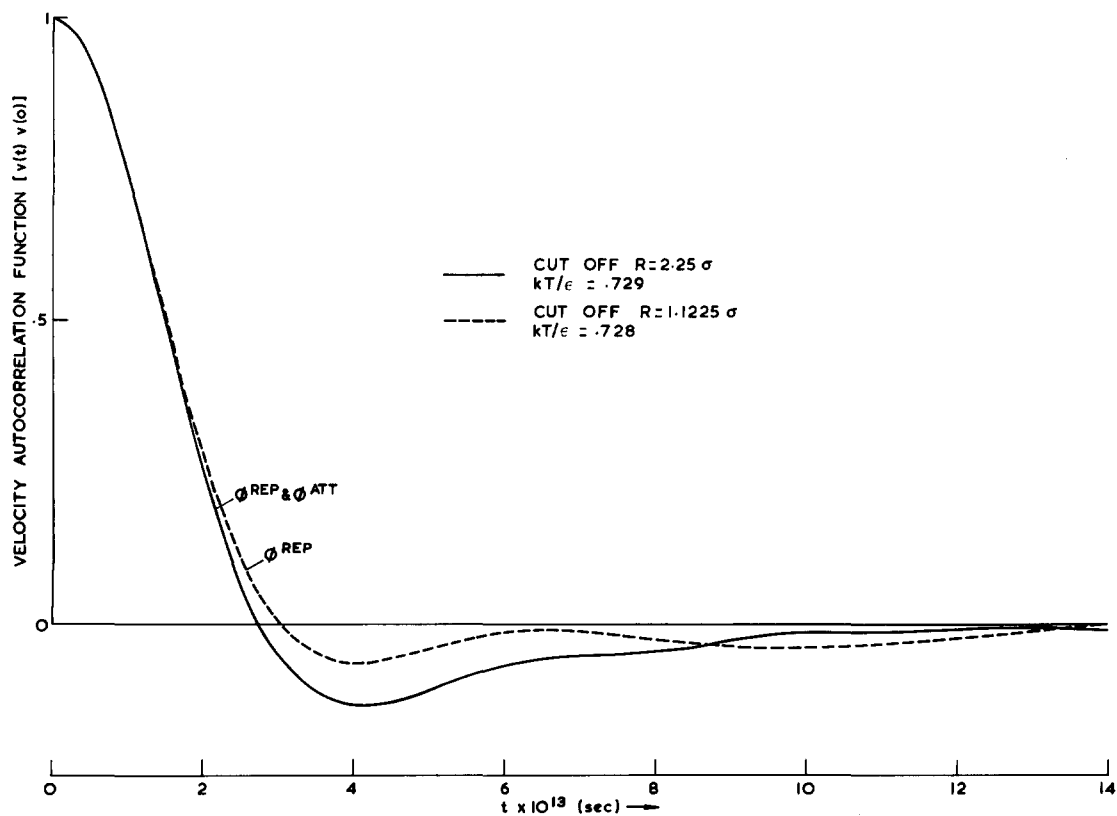
Acknowledgements

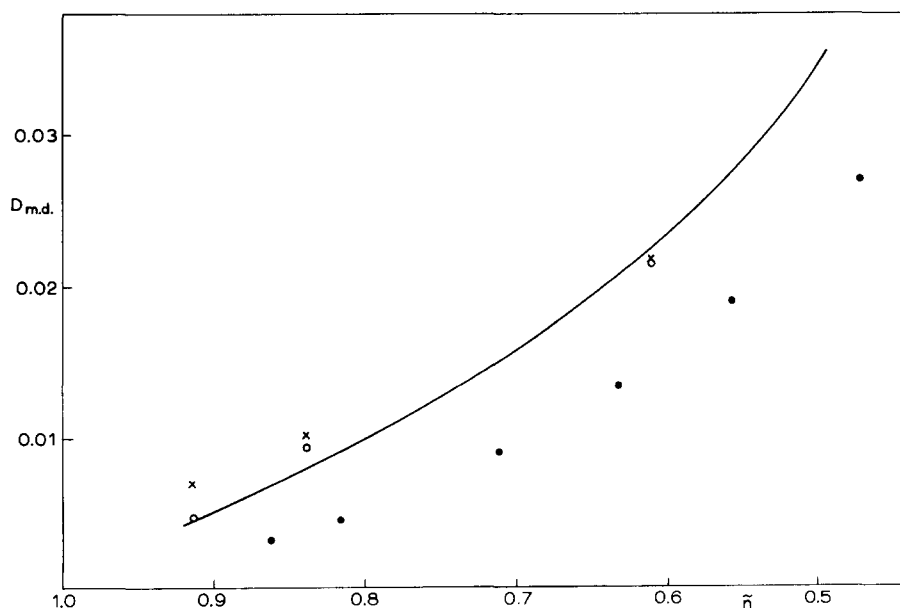Fig. 3. Velocity autocorrelation function for particle in the two potentials of fig. 1.

Fig. 4. Self-diffusion constant for various potentials: ● R^{-12} potential; o Lennard-Jones potential cutoff at $R = 2.25\,\sigma$ for three state points of table 1; × the same, cutoff at $R = 1.1255\,\sigma$; — The empirical formula of Levesque and Verlet [6] for Lennard-Jones potential for $kT/\epsilon = 1.0$.

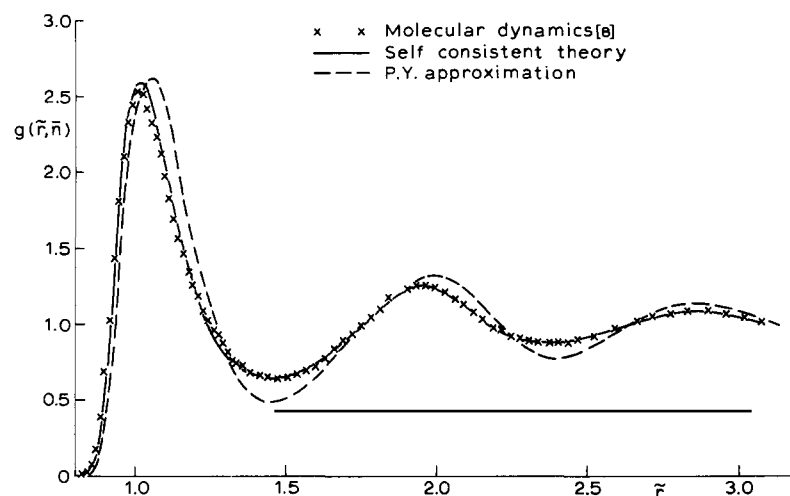Fig. 5. Comparison of Percus–Yevick and Hutchinson and Conkie [1] theories for g $(\tilde{r})$ with molecular dynamics for R^{-12} repulsive potential, $\tilde{n} = 0.71$ $[\tilde{r} = \sigma(\epsilon/kT)^{\frac{1}{12}}]$.
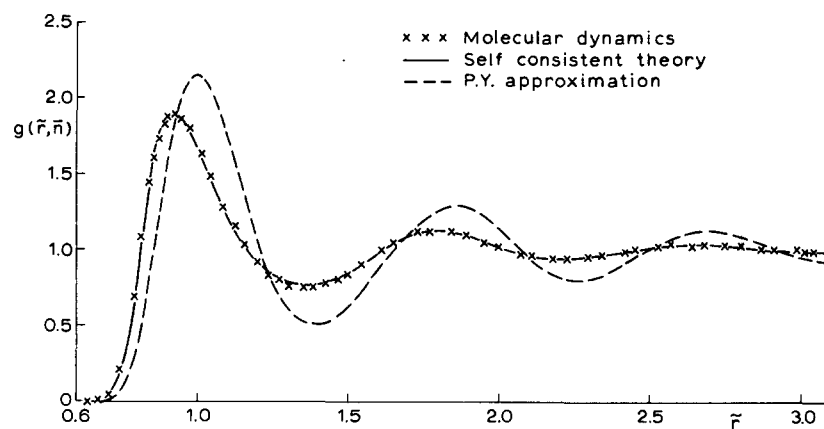

Fig. 6. Comparison of theory of $g(\tilde{r})$ with molecular dynamics for R^{-6} repulsive potential, $\tilde{n} = 0.91$ $[\tilde{r} = \sigma(\epsilon/kT)^{\frac{1}{6}}]$.

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