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A novel simulation model for three-body dispersion interactions

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Abstract. We present a novel molecular dynamics simulation technique, which accounts for both two- and three-body dispersion interactions. This technique is a unified approach of molecular dynamics and quantum mechanical variational methods, in the spirit of the Car–Parrinello method (1985 *Phys. Rev. Lett.* **55** 2471). We use a highly simplified model for the electronic structure of the atoms, which is, nevertheless, sufficient to correctly reproduce the London two-body, and the Axilrod–Teller three-body dispersion forces in an appropriate limit. The advantage of this new method is that it allows for a consistent treatment of both dispersion damping and periodic boundary conditions at the pair *and* three-body levels.

1. Introduction

The *accurate* representation of dispersion effects in computer simulation models presents a number of difficulties. In classical simulations, with potentials expressed as functions of internuclear separations, it necessitates the introduction of three-body terms. Gas-phase studies of the pair dispersion potential reveal important short-range corrections to the familiar asymptotic forms, such as the C_6/R^6 dipole–dipole term, due to overlap of the charge clouds, which lead to a ‘damping’ of the dispersion interaction [2]. They also show important contributions due to higher-order (dipole–quadrupole etc) terms. At the three-body level, although the asymptotic triple–dipole term is well known (the Axilrod–Teller (A–T) potential [3]) the effect of damping is uncharacterized and the higher-order terms are not easily represented. Furthermore, even the introduction of the A–T term presents the technical problem of truncating the triple sum in condensed-phase calculations: this appears to have precluded molecular dynamics (MD) studies. It is therefore difficult to perform calculations in which the treatment of three-body effects is consistent with that of dispersion at the pair level. This difficulty is not surmounted by recourse to *ab initio* MD methods [1]; at the present time, the available electronic density functionals do not include dispersion correctly [4].

Interest in the three-body terms has been stimulated by recent accurate measurements of the structure factor of atomic fluids [5]. More generally, it is often thought that other (e.g. thermodynamic) manifestations of three-body effects are sufficiently well accounted for by the use of *effective* pair potentials. However, the state dependence of such potentials [6] and their non-uniqueness are less frequently recognized [7]: for a given three-body interaction a different effective pair potential is required to reproduce the internal energy

and the pressure (and structure) at a single state point. The problem for simulation thus arises when a pair dispersion term has been accurately characterized, by electronic structure calculations or experiment on the dimer. At present, there is no *consistent* way of introducing its three-body counterpart into a bulk-phase calculation so as to retain a fully quantitative description. The problem is pressing in modelling ionic systems [8] (*inter alia*), where dispersion effects are, in absolute terms, quite large.

For these reasons we have been exploring simulation methods for a model system which permits a fully self-consistent treatment of dispersion effects at the two- and three-body level, alongside a conventional pair potential description of other interactions, such as short-range repulsion. In this paper we will describe calculations which yield the asymptotic dipole–dipole/triple-dipole terms only, but the method is straightforwardly generalized to deal with all the difficulties raised above [9].

2. A simplified quantum mechanical model

Dispersion is a quantum mechanical effect and cannot be recaptured by the introduction of additional classical dipoles, as with the induction effect [10]. For our purposes it is best viewed as the reduction in the zero-point energy of the electrons in a collection of atoms due to their mutual correlation. At large separations the electronic Hamiltonian of a collection of identical atoms [11] is given by

$$\hat{H} = \sum_i \hat{H}_i - \sum_{i<j} \hat{\boldsymbol{\mu}}_i \cdot \mathbf{T}_{ij} \cdot \hat{\boldsymbol{\mu}}_j \quad (1)$$

where the summation indices go over all atoms; in (1), \hat{H}_i is the single-atom Hamiltonian of atom i , $\hat{\boldsymbol{\mu}}_i$ its dipole moment operator and $T_{ij}^{\alpha\beta}$ a component of the dipole–dipole interaction tensor [11] between atoms i and j . We exploit a highly simplified model for the electronic structure of each atom, which is represented by a *single*, distinguishable quantum particle. This particle can only be in four possible states: a ground state (or ‘s’-type state, $|s(i)\rangle$) which is completely symmetric, and three excited ‘p’ states ($|p_x(i)\rangle$, $|p_y(i)\rangle$, $|p_z(i)\rangle$). This is the minimum set of states which allow for transitions from the ground state, via the *dipole* operator, to excited states. Simultaneous dipole transitions on different atoms give rise to dispersion interactions. The difference in energy between the s and p states is denoted u_1 ($u_1 = E_p - E_s$) and the dipole matrix elements are specified by a single parameter μ :

$$\langle s(i) | \hat{\boldsymbol{\mu}}_i | p_\alpha(i) \rangle = \mu \mathbf{e}_\alpha. \quad (2)$$

A standard perturbation calculation (atom in electrical field) yields that

$$\mu^2 = \frac{1}{2} \alpha_1 u_1 \quad (3)$$

where α_1 is the polarizability of the atom. Treating the dipole–dipole interaction in (1) as a perturbation, we get to third order in the perturbation expansion for the energy [11] of N atoms, by use of (2) and (3),

$$E = E_0 + \sum_{i<j} \frac{C_6}{R_{ij}^6} + \sum_{i<j<k} C_9 \frac{(1 + 3 \cos \gamma_i \cos \gamma_j \cos \gamma_k)}{R_{ij}^3 R_{ik}^3 R_{jk}^3} \quad (4)$$

with

$$C_6 = -\frac{3}{4} \alpha_1^2 u_1 \quad C_9 = \frac{9}{16} \alpha_1^3 u_1. \quad (5)$$

In equation (4), the first term, E_0 , is the energy of the non-interacting atoms (which in the following we put to zero), the second term is the two-body London dispersion energy

[12] and the last term is the three-body A–T potential [3], where γ_i, γ_j and γ_k are the interior angles of the triangle formed by the atoms i, j , and k . From equations (3) and (5) it follows that we can determine the parameters μ and u_1 of the model atom from the physical parameters α_1 and the pair dispersion coefficient C_6 only. Note that the three-body coefficient C_9 is then determined as well, i.e. we have the relationship $C_9 = \frac{3}{4}\alpha_1 C_6$, which is known to be correct within a few per cent [13].

The classical forms (4) may be implemented directly in simulations (though the three-body term may create practical difficulties with respect to defining cut-offs in periodic boundary conditions). Our purpose is to introduce a method which will deal with more complex interaction Hamiltonians than (1), and therefore deal with the difficulties mentioned at the outset. To this end, we re-cast the above calculations in a variational form, in order that we might exploit the Car–Parrinello (C–P) [1] methodology for adiabatic dynamics.

3. Variational approach

In the variational description, the total electronic ground state of the system will be represented by a wavefunction $|\psi\rangle$ which is an expansion about the non-interacting ground state over all possible *pairs* of excited states:

$$|\psi\rangle = |\psi_s\rangle + \sum_{i \neq j} \sum_{\alpha\beta} c_{ij}^{\alpha\beta} |\psi_{ij}^{\alpha\beta}\rangle \quad (6)$$

where

$$\psi_s = s(1)s(2) \cdots s(N) \quad \psi_{ij}^{\alpha\beta} = s(1)s(2) \cdots p_\alpha(i) \cdots p_\beta(j) \cdots s(N)$$

i.e. we use a limited (only doubly excited) configuration interaction scheme (DCI). If the Hamiltonian of the system is given by (1), we can evaluate the energy:

$$E^{\text{DCI}}(\{c\}, \{\mathbf{R}\}) = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} = \sum_{ij} \frac{e_{ij}}{n} + \sum_{ijk} \frac{e_{ijk}}{n} \quad (7)$$

with

$$e_{ij} = \sum_{\alpha\beta} \left[4u_1 (c_{ij}^{\alpha\beta})^2 - 2\mu^2 T_{ij}^{\alpha\beta} c_{ij}^{\alpha\beta} \right] \quad (8)$$

$$e_{ijk} = -4\mu^2 \sum_{\alpha\beta\gamma} T_{ij}^{\alpha\beta} c_{ik}^{\alpha\gamma} c_{jk}^{\beta\gamma} \quad (9)$$

and where n is the normalization factor ($n = 1 + 2 \sum_{\alpha\beta ij} (c_{ij}^{\alpha\beta})^2$). The first term in e_{ij} , equation (8), is the energy required to excite both atoms i and j , in the absence of any interaction. The second term is the corresponding gain in energy because of the dipole–dipole interaction present between the atoms. Note that the sum of these two contributions will always have a minimum for $c_{ij}^{\alpha\beta} \neq 0$, i.e. there is an attractive pair interaction energy for *all* distances. There is however a three-body term e_{ijk} , equation (9), present as well, which follows from correlated excited states in *both* the bra and ket of the $\langle \psi | \hat{H} | \psi \rangle$ term.

The ground-state energy is the minimum of (7) with respect to the coefficients. At the *pair* level (omitting e_{ijk}), this can be calculated exactly, giving

$$\min E^{\text{DCI}}(\{c\}, \{\mathbf{R}\}) = u_1 - u_1 \sqrt{1 + (6\mu^4/u_1^2) \sum_{i < j} R_{ij}^{-6}}. \quad (10)$$

Expanding the square root would seem to give, to lowest order in the distance, the perturbation expression (4) and (5) for the pair dispersion interaction; however, this would

only be correct for a system of *two* atoms; for a system of N atoms, it is obvious that the energy (10) would scale like \sqrt{N} instead of N , in other words, the energy is size inconsistent. This is a well-known feature of truncated configuration interaction methods of many-particle systems [14]. In principle, for an N -atom system the wavefunction should contain up to N correlated excitations in order to get a size-consistent energy.

This problem is circumvented by using the ‘coupled-pair approximation’ (CPA), introduced into electronic structure theory by Ahlrichs and Scharf [15] in order to achieve a size-consistent variational DCI calculation. In our context, this consists of replacing the normalization factor n in (7) by a *partial* normalization factor n_{ij} :

$$E^{\text{CPA}}(\{c\}, \{\mathbf{R}\}) = \sum_{ij} \frac{e_{ij}}{n_{ij}} + \sum_{ijk} \frac{e_{ijk}}{(n_{ik}n_{jk})^{1/2}}. \quad (11)$$

The best choice for the factor n_{ij} depends on the problem at hand. We follow the suggestion given by Ahlrichs and Scharf [15], which translates for our model to

$$n_{ij} = 1 + \sum_{\alpha\beta} \sum_l ((c_{il}^{\alpha\beta})^2 + (c_{lj}^{\alpha\beta})^2).$$

The result is a variational function (11) which at its minimum achieves a size-consistent value, which is close to that obtained from the the perturbation expression (4) for our problem, as we will demonstrate next.

Table 1. The ratio of the variational energy E_{var} to the perturbation energy E_{per} , at the two-body level. In the second column E_{var} is given as the minimum of the truncated CI expression (7); in the third column E_{var} is the minimum of expression (11); E_{per} is given by equation (4). The system studied was argon at a reduced density of about 0.75.

| Number of atoms | $E_{\text{var}}/E_{\text{per}}$ | |
|--------------------|---------------------------------|----------|
| | DCI (7) | CPA (11) |
| 2 | 0.999 | 0.99999 |
| 8 | 0.995 | 0.99954 |
| 27 | 0.977 | 0.99922 |
| 64 | 0.942 | 0.99907 |
| 125 | 0.890 | 0.99898 |
| 216 | 0.827 | 0.99892 |
| 343 | 0.736 | 0.99887 |
| 512 | 0.671 | 0.99884 |

The functional (11) has the useful property for testing that the e_{ijk} -term contains all the three-body effects; we therefore first examine the energies obtained from the simplified functional with this term omitted and compare the results with the standard perturbation energies for pair dispersion only ($\sum_{i<j} C_6 R_{ij}^{-6}$). The results are shown in table 1 for various system sizes. It is clearly demonstrated that, at the pair level, the expression for the energy in the CPA (11) is size-consistent and its minimum very close to the perturbation theory result; this is in contrast to (7).

We next consider the energy of a triplet of atoms (figure 1). The total energy of the triplet (from equation (11)) less the pair dispersion energy of all pairs should agree with the A–T energy if the functional gives results in agreement with perturbation theory. The figure shows excellent agreement with regard to both the functional form and magnitude of the A–T term. Calculations on larger clusters indicate that the total three-body energy is size consistent and agrees to at least 95% of the A–T energy for system of up to 125 atoms.

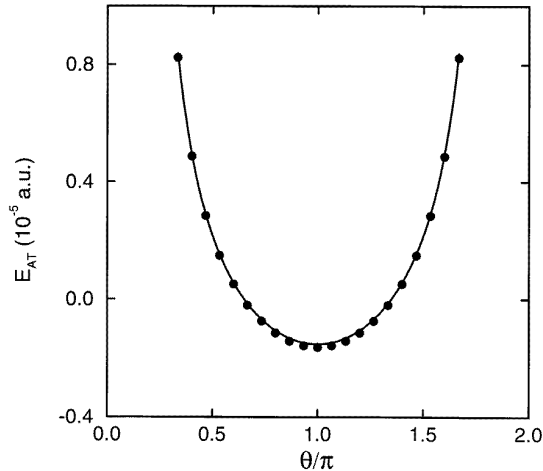


Figure 1. The three-body energy of an interacting triplet, obtained from the minimum of the CPA functional (11) (points), compared with the Axilrod–Teller energy (line) as the internal angle θ is varied to pass from the equilateral triangle to the linear geometry. The distance of the particles in the triangle was set to 1.2σ .

4. *Ab initio* molecular dynamics and results

We may now devise an MD simulation method in which the expansion coefficients in the wavefunction (6) are treated as additional degrees of freedom in the Car–Parrinello sense [16]. Equations of motion for the expansion coefficients are derived from the Lagrangian formulation of classical mechanics, with the electronic energy (11) playing the role of a potential. To perform molecular dynamics the coefficient equations of motion may be combined with equations of motion for the atomic positions and integrated simultaneously in time with the coefficients maintained at the adiabatic values, as in the standard C–P method [16]. This proved straightforward to implement; full details will be given elsewhere [9]. We describe results from a simulation with 125 argon atoms, using periodic boundary conditions. The repulsive part of interaction is modelled by a classical $4\epsilon\sigma^{12}/R^{12}$ potential and the C_6 -coefficient, which determines that the electronic parameters in the model atom, is set to $-4\epsilon\sigma^6$, where ϵ and σ are the familiar Lennard-Jones parameters. The system is held at a constant temperature (100 K) by applying a thermostat; the particle density was set to 0.70 in reduced units. We used a time-step of about 1.2 fs, which is about six times smaller than what would be normally used in a classical MD simulation. The run lasted 10 ps.

To demonstrate consistency with previously established fluid properties with the normal two- and three-body perturbation theory potentials we make contact with theoretical results obtained by Attard [17] for the three-body contribution to the effective pair interaction energy, denoted $u_{\text{eff}}(R)$. This is obtained in the simulation by considering a pair of atoms i and j at separation R and averaging $\sum_{k \neq i, j} e_{ijk} \delta(R_{ij} - R)$ over the course of the simulation run. This averaging can be done conveniently because the geometry in e_{ijk} only appears at the *pair* level (i.e. via \mathbf{T}_{ij}). Theory [18] shows that at large separations the three-body contribution to the effective pair potential goes as $(8/9)\pi\rho C_9 R^{-6}$; in figure 2, we plot $u_{\text{eff}}(R)/(C_6 R^{-6})$ and compare with the same quantity extracted from the figure in Attard’s paper (at $\rho^* = 0.7$, $T = 100$ K) [17]. Note that the three-body contribution to the effective

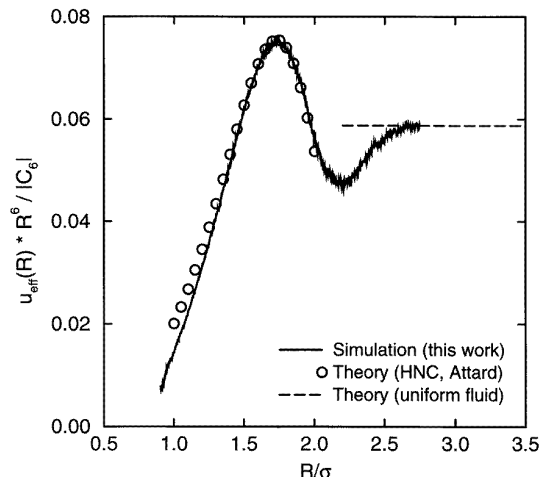


Figure 2. The effective pair potential u_{eff} reduced from the three-body A–T potential. The solid line is the result obtained in a full three-body simulation, and is compared with Attard’s theoretical result [17] and the theoretical large R -limit (dashed). For argon at $\rho^* = 0.7$, $T = 100$ K.

pair interactions is of the order of 6% of the true (C_6R^{-6}) pair potential for argon at this density. The close correspondence between the values of u_{eff} obtained in this work, and Attard’s result, and the limiting value leave no room for doubt that three-body interactions in our simulation are reproducing A–T behaviour very closely.

We finally note that one of the assets of the present simulation model is that the three-body energy term (9) contains the geometry of the atoms only at the *pair* level. This implies that the three-body energy can be treated with respect to periodic boundaries and dispersion damping, consistent with the pair interactions. This feature opens the way for a quantitative study of three-body dispersion effects in bulk systems.

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