Solvation effects in the CF1 central force model of water: Molecular dynamics simulations

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ABSTRACT

Molecular dynamics simulations are used to study the properties of water modelled by the CF1 potential. The majority of the simulations are undertaken in the isothermal-isobaric ensemble. A short review of constant pressure and temperature molecular dynamics techniques is presented with particular reference to their application to the CF1 model of water. The shifted force CF1 model of water is studied. By shifting the force and potential curves in such a way as to remove the long-range Coulomb tail, it is possible to form short-range potentials which capture a few features of the actual CF1 potentials.

INTRODUCTION

Molecular dynamics is a common computational technique. In this paper we discuss certain aspects of molecular dynamics as it relates to our research interests on solvation effects in CF1 water. In the next section we present a short review of constant pressure molecular dynamics algorithms which allow us to compare our simulation results to experiment with greater ease. The remaining sections show the application of a shifted force technique which allows rapid equilibration of the simulation box by generating a set of short range CF1 potentials.

CONSTANT PRESSURE MD SIMULATIONS

This section summarises the various methods which exist in the literature for performing simulations in which the pressure is kept constant. All discussion is related to systems of atomic nature, however they can be readily generalised to molecular systems.

The Andersen Extended System Method

The first simulations involving constant pressure were performed by Andersen[1]. In a constant pressure simulation the volume of the system will fluctuate while the pressure remains constant. These fluctuations are introduced into the system by treating the volume as an additional dynamical variable. The system then remains at constant pressure by expanding or contracting isotropically.

The particle's position, r_i, is replaced by a scaled co-ordinate, s_i, which is defined

as

$$s_i = r_i/V^{\frac{1}{3}} \ . \tag{1}$$

The Lagrangian for the system is then simply the kinetic energies of the particles and the piston minus the potentials due to the particle interactions, ϕ, and the external pressure and is given by

$$\mathcal{L} = \frac{1}{2}mV^{\frac{2}{3}}\sum_{i=1}^{N}\dot{s}_i \cdot \dot{s}_i - \sum_{i<j}\phi(\frac{1}{3}Vs_{ij}) + \frac{1}{2}M\dot{V}^2 - P_0V \ , \tag{2}$$

where V is the volume, P_0 is the external pressure, m is the particle mass, $s_{ij} = s_i - s_j$ and M is the mass of the piston keeping the pressure constant. The equations of motion generated by this Lagrangian are then given by

$$\frac{dr_i}{dt} = \frac{p_i}{m} + \frac{1}{3}r_i\frac{d(lnV)}{dt} \ , \tag{3}$$

$$\frac{dp_i}{dt} = -\sum_{j\neq i}\hat{r_{ij}}\phi'(r_{ij}) - \frac{1}{3}p_i\frac{d(lnV)}{dt} \text{ and} \tag{4}$$

$$M\frac{d^2V}{dt^2} = -P_0 + \frac{1}{V}(\frac{2}{3}\sum_i\frac{p_i \cdot p_i}{2m} - \frac{1}{3}\sum_{i<j}r_{ij}\phi'(r_{ij})) \ , \tag{5}$$

where p_i is the particle momentum and $r_{ij} = r_i - r_j$. In the limit that the mass of the piston becomes infinite these equations reduce to the microcanonical case above. Other than this restraint the mass of the piston has no effect on the averages that are calculated from the trajectories. These equations produce trajectories in the isoenthalpic-isobaric ensemble. By combining this method with the constant temperature method explained in the same paper it is possible to generate trajectories in the NPT ensemble.

Parrinello and Rahman[2] generalised the method of Andersen to take into account full flexibility of the MD cell. In their method the edges of the cell are formed by three (variable) vectors $\vec{a}, \vec{b}$ and $\vec{c}$ which are defined in a fixed reference co-ordinate

system. The volume of the cell is then given by taking the determinant of the matrix $\underline{\mathrm{h}} = (\vec{a}\vec{b}\vec{c})$. The position of a particle i is given by $r_i = \xi_i\vec{a} + \eta_i\vec{b} + \zeta_i\vec{c} = \underline{\mathrm{h}}s_i$ where s_i is a column vector given by $(\xi_i, \eta_i, \zeta_i)^t$ where the superscript t denotes the transpose. The Lagrangian for the system is given by

$$L = \frac{1}{2}\sum_i \dot{s}_i{}^t \underline{\mathrm{G}} \dot{s}_i - \sum_i \sum_{j>i} \phi(r_{ij}) + \frac{1}{2} M \mathrm{Tr}(\dot{\underline{\mathrm{h}}}^{\mathrm{t}} \dot{\underline{\mathrm{h}}}) - \mathrm{P}_0 \mathrm{V} \ , \tag{6}$$

where $\underline{\mathrm{G}} = \underline{\mathrm{h}}^t \underline{\mathrm{h}}$. This Lagrangian can then be used to generate the equations of motion for this system which when solved generate trajectories which sample the NPH ensemble [3].

The Constraint Method

Another major class of constant pressure algorithms is known as the *constraint methods*[4]. In these methods, modified equations of motion are used which generate trajectories in which the instantaneous pressure is a constant of the motion as opposed to the Andersen method where the system takes time to respond to the changes in the pressure resulting in pressure fluctuations.

Evans and Moriss[5] showed that the trajectories in the NPT ensemble of Andersen are not smooth. They suggested the constraint method in an attempt to counter this, to keep the pressure exactly constant and to remove the "unknown" parameters that are part of that system.

The method uses a Hamiltonian defined by

$$H = H_0 + \dot{\epsilon} \sum_i r_i \cdot p_i \ , \tag{7}$$

where H_0 is the constant NVE Hamiltonian. Solving Hamilton's equations (and including the constant temperature formalism) gives the equations of motion

$$\dot{r}_i = \frac{p_i}{m} + \dot{\epsilon} r_i \text{ and} \tag{8}$$

$$\dot{p}_i = F_i - \dot{\epsilon} p_i - \alpha p_i \ . \tag{9}$$

where F_i is the force on particle i, α is the temperature damping coefficient and $\dot{\epsilon}$ is the dilation rate of the system which is defined by the equation

$$\dot{V} = 3V\dot{\epsilon} \ . \tag{10}$$

These equations generate trajectories in the isothermal-isobaric ensemble.

The Berendsen Method

The constraint method has disadvantages which were highlighted Berendsen[6]. An unstabilized drift in the pressure or temperature can occur, as the reference temperature and pressure do not appear in the formalism. Also the Hamiltonian is unphysical, although the method is consistent with Gauss' Principle of Least Constraint. Berendsen goes on to describe another method for constant pressure simulation. In this method, an extra term is added to the equations of motion to change the pressure

$$\frac{dP}{dt} = \frac{P_0 - P}{\tau_P} \ , \tag{11}$$

where P_0 is the desired pressure of the system and τ_P is a time constant for the pressure. This results in the volume of the box being scaled by a factor of χ and the centre-of-mass coordinates of each molecule by $\chi^{\frac{1}{3}}$ where

$$\chi = 1 - \frac{\beta \Delta t}{3\tau_P}(P_0 - P) \ , \tag{12}$$

and β is the isothermal compressibility.

Refining The Constant Pressure Methods

Over subsequent years the method of Anderson and Nosé was refined and developed by Hoover[7], Wentzcovitch[8], Lill and Broughton[9] and Melchionna, Ciccotti and Holian [10] who dealt with technical aspects such as modular invariance, multiple thermostats etc. The most recent formulation of the extended system method is given by Martyna, Tobias and Klein[11] who claimed that there were still inconsistencies in the formulation of the equations of motion for constant pressure MD. In particular they claimed the various formalisms do not generate trajectories from a true isothermal-isobaric ensemble. Melchionna et al [12] responded to the Martyna et al paper to show that although the criticisms were valid for earlier formulations of the extended system method, their formulation does generate a true constant NPT ensemble.

Recently there have been further developments. Bernasconi[13] combined Carr-Parrinello molecular dynamics with the Parrinello-Rahman method for changing cell shape to generate *ab initio* constant pressure molecular dynamics. Feller et al[14] proposed an new method called the Langevin Piston method which overcomes certain shortcomings of the Andersen and Berendsen methods by adding an extra Langevin term to the Andersen equations. Finally Melchionna and Ciccotti[15] have developed a method for molecular systems which scales the atomic co-ordinates rather than the molecular centre of mass.

Each method has its own advantages and disadvantages. The extended system

methods produce well-defined trajectories but experience undesirable oscillations in the pressure. The constraint methods remove the oscillations but at the expense of utilizing an unphysical Hamiltonian and having a potentially unstabilized drift in the pressure. Finally the Berendsen method while overcoming the above disadvantages produces trajectories in an undefined ensemble. The best method appears to be that described by Martyna et al[11] or equivalently the method of Melchionna et al[10] which appear to have consolidated the best of the various methods and reformulated the equations to remove some of the more technical inconsistencies.

APPLICATION TO CF1 MODEL OF WATER

This work simulates the interaction between 108 water molecules which interact as defined by the CF1 potential of water. These potentials were originally derived by Stillinger and Rahman [16] and were later modified by Duh and Haymet[17]. The CF1 potentials have two distinct parts – a Coulomb term which falls off as the inverse power of distance and various short range terms which fall off rapidly to zero.

In a simulation the long range forces are calculated using the Ewald summation method[4] which is a computationally demanding part of the program. The majority of the run time of an MD simulation is spent in the calculation of the forces. The inclusion of the long range forces is necessary for a correct treatment of the system. However during equilibration of a system the accuracy of the results is much less important than the time taken to reach equilibrium. In this section we present a method where the expensive Ewald sums can be temporarily removed in order that a system may rapidly

approach an approximate equilibrium point. Once equilibrated the Ewald sums would be added back in to complete the equilibration and then generate accurate trajectories for analysis.

In order to remove the need for the Ewald summation we require a set of potentials which approximate the full CF1 potentials. The full CF1 potentials and forces are shown in Figure 1. It can be seen that there is still a significant potential at the point at which the potentials are cut-off. In order to be truly effective both potentials and forces must smoothly and continuously move to zero at the cut-off point. This was achieved by applying the method of shifted force potentials [18]. Figure 1 also shows the shifted-force potential curves for the CF1 model of water and compares them to the original CF1 potentials. The new shifted force potentials and forces can be seen to go smoothly to zero at the cut-off point of 7 Å.

The difference between the potentials was checked by running simulations using the original version of the code (full CF1 potentials by Ewald summation) and the modified version of the code (short ranged shifted force CF1 potentials). The average energy of a water molecule was found to differ only by 0.5 %. It is important that this difference be as small as possible to avoid an excessive amount of work when switching between the full Ewald calculation and the shifted-force calculation. If the energies were significantly different the simulation would need a considerable time to re-equilibrate to the new potentials after such a switch occurs. This would negate any benefit obtained by allowing the system to approach equilibrium rapidly by equilibrating in the shifted-force system.

Two simulations were performed to compare the effect of shifting potentials on

the calculated averages. The simulations were well equilibrated in each system by simulating for at least 5 ps before the production runs were undertaken. The production runs were 5 ps in duration with a time step of 0.05 fs. The simulations were undertaken in the standard MD NVE ensemble with averages collected every 2 fs. The average temperature of each system was close to 300 K being about 311 K in the case of the shifted force potentials and 310 K in the case of the full potentials.

The averages obtained from each run were similar. Plots of the energy and temperature for each system are shown in Figures 2 and 3. The energy fluctuations in the shifted-force system are much larger than in the full CF1 potentials. This makes it undesirable for using the shifted-force potentials for accumulating production run averages but has no effect on the usefulness of the system for rapidly approaching equilibrium. The average energy of the shifted-force potentials is also slightly higher than the CF1 potentials but not to such an extent that prolonged re-equilibration would be required after shifting back to CF1 potentials. Pair correlation functions were also collected for both systems as a check that the solution was in equilibrium and also to confirm that the two models give the same average structure for water. The g(r) were found to be almost exactly identical and are shown in Figure 4.

Two similar simulations were performed to compare the difference in run-time. Each simulation was for 0.5 ps with a time step of 0.05 fs. Averages were accumulated every 40 steps (2 fs) and the simulation was done in the NVE ensemble. The calculation with the shifted force potentials was 2.77 times faster than the full calculations.

CONCLUSIONS

The shifted force potentials of CF1 water are a viable alternative to the full potentials especially for the purpose of equilibrating the system. Our results have shown that there are only minor differences in the averages generated by the two systems allowing easy switching between the two sets of potentials. The pair correlation functions for each system confirm that the shifted-force potentials do indeed give the correct structure for water. Simulation with the shifted-force potentials is 2.77 times faster than with the full potentials. This encourages the use of the shifted force potentials as a means of equilibrating the system quicker before the full-potentials are used to generate exact averages.

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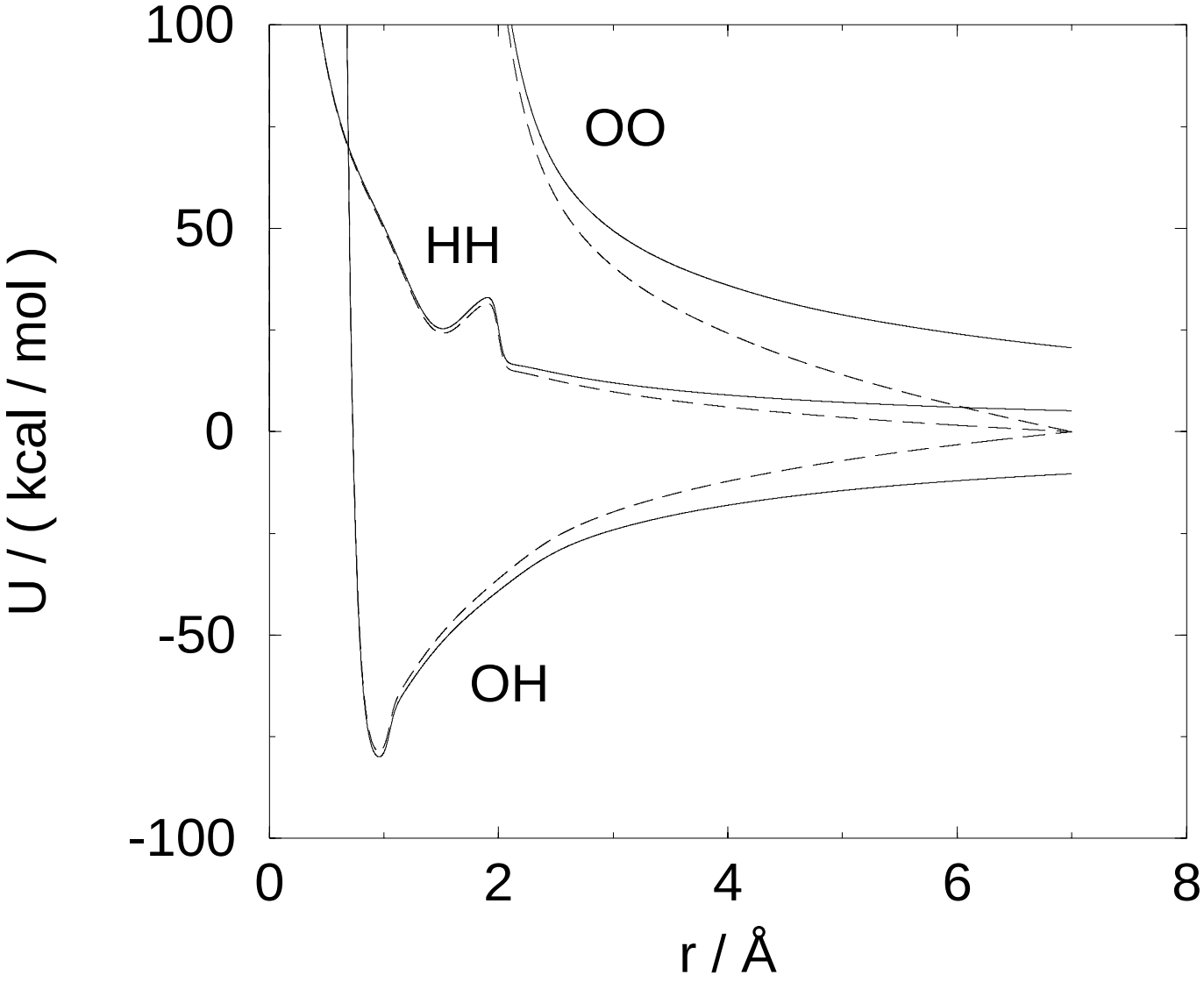
Figure 1: Potential functions for the CF1 model of water. The solid line represents the full CF1 potentials. The dashed line represents the shifted force potentials.

Figure 2: Results for a 5 ps simulation in the NVE ensemble using the full CF1 potentials. Plots of both temperature and energy per molecule with respect to time are shown. The simulation involves a time step of 0.05 fs and instantaneous values were accumulated every 2 fs.

Figure 3: Results for a 5 ps simulation in the NVE ensemble using the shifted force potentials. All other details are as for Figure 2.

Figure 4: Pair correlation functions (OH, HH and OO from bottom to top) for the full CF1 potentials and the shifted force potentials (squares). The HH and OO functions are shifted up by 2 and 4 respectively for clarity.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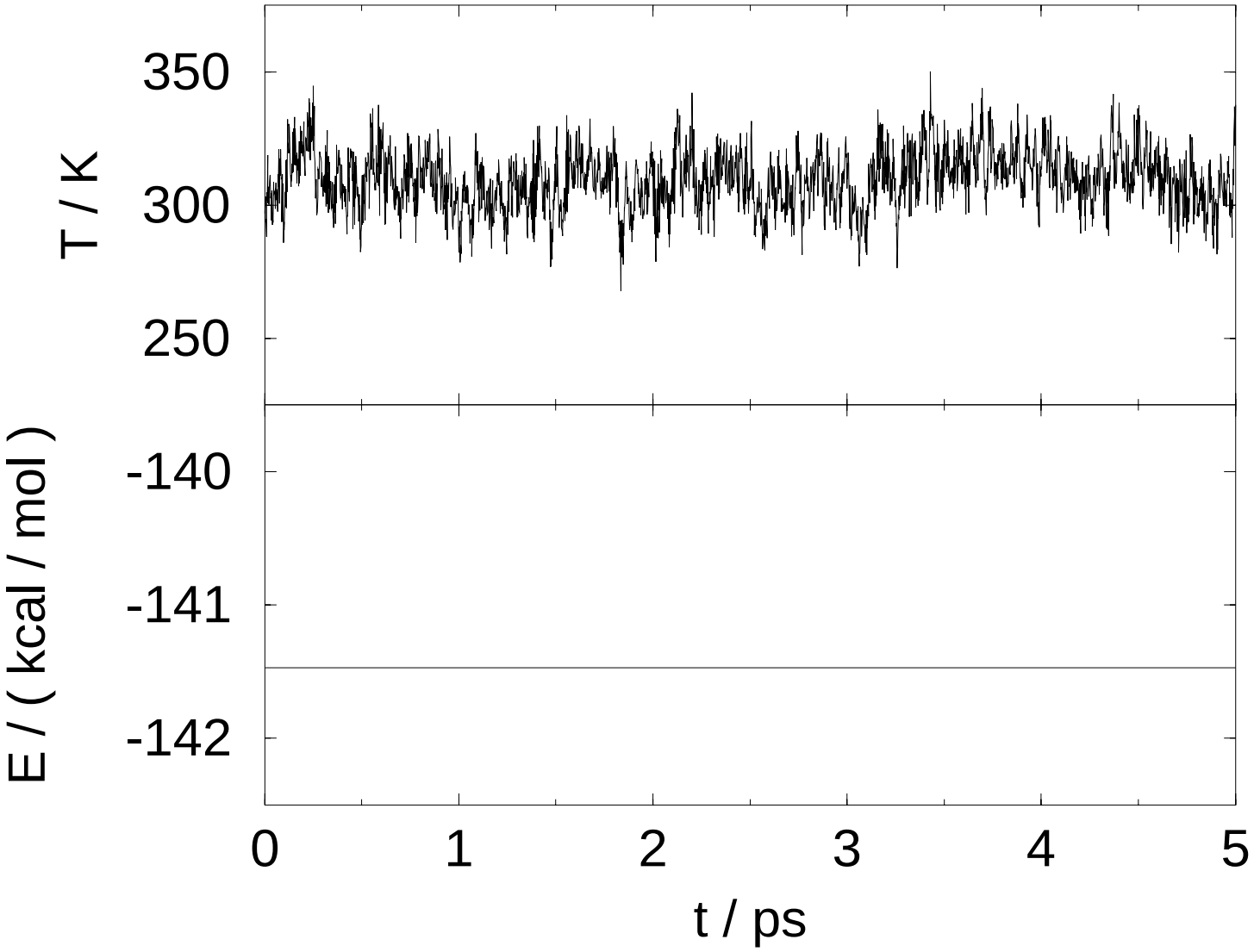
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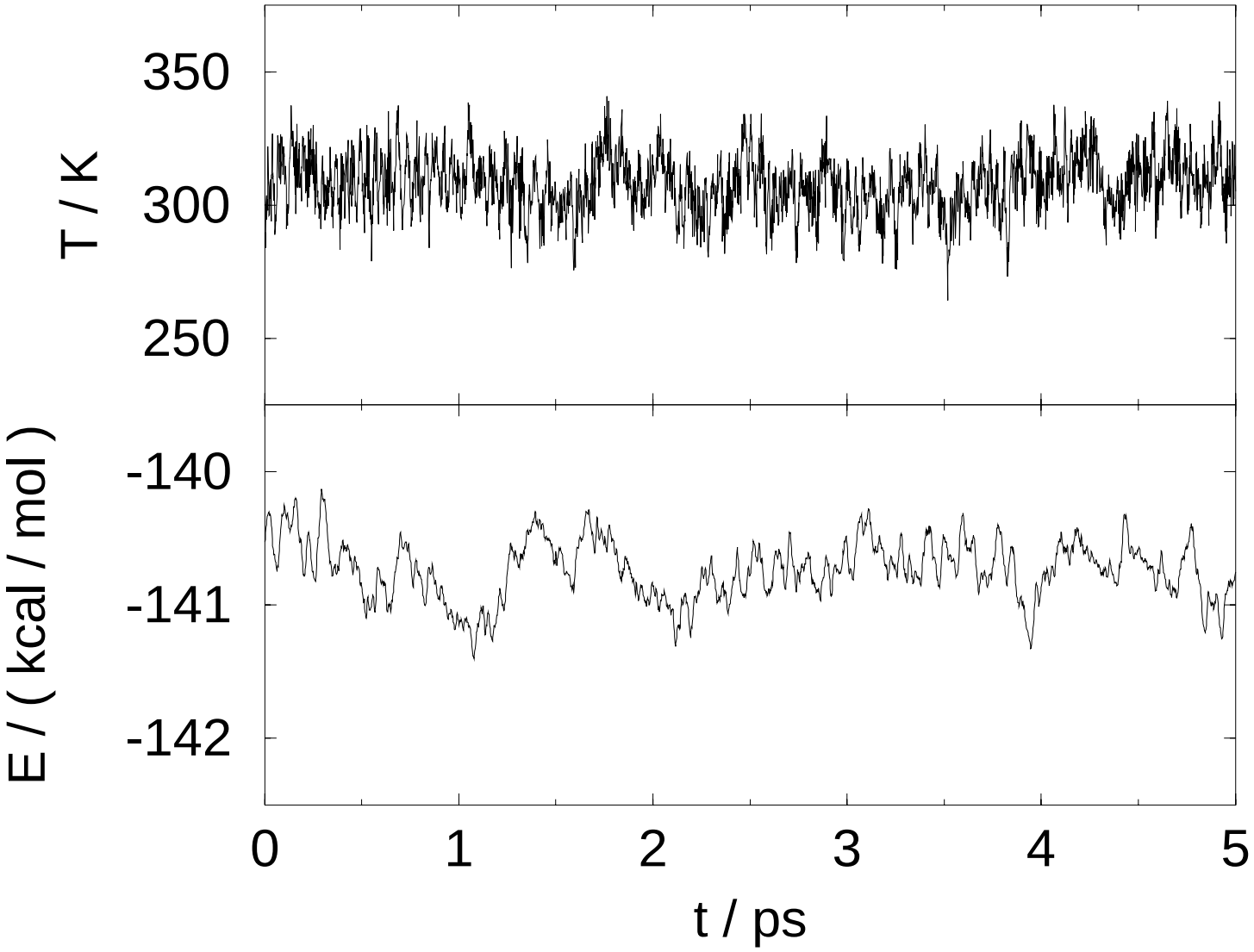
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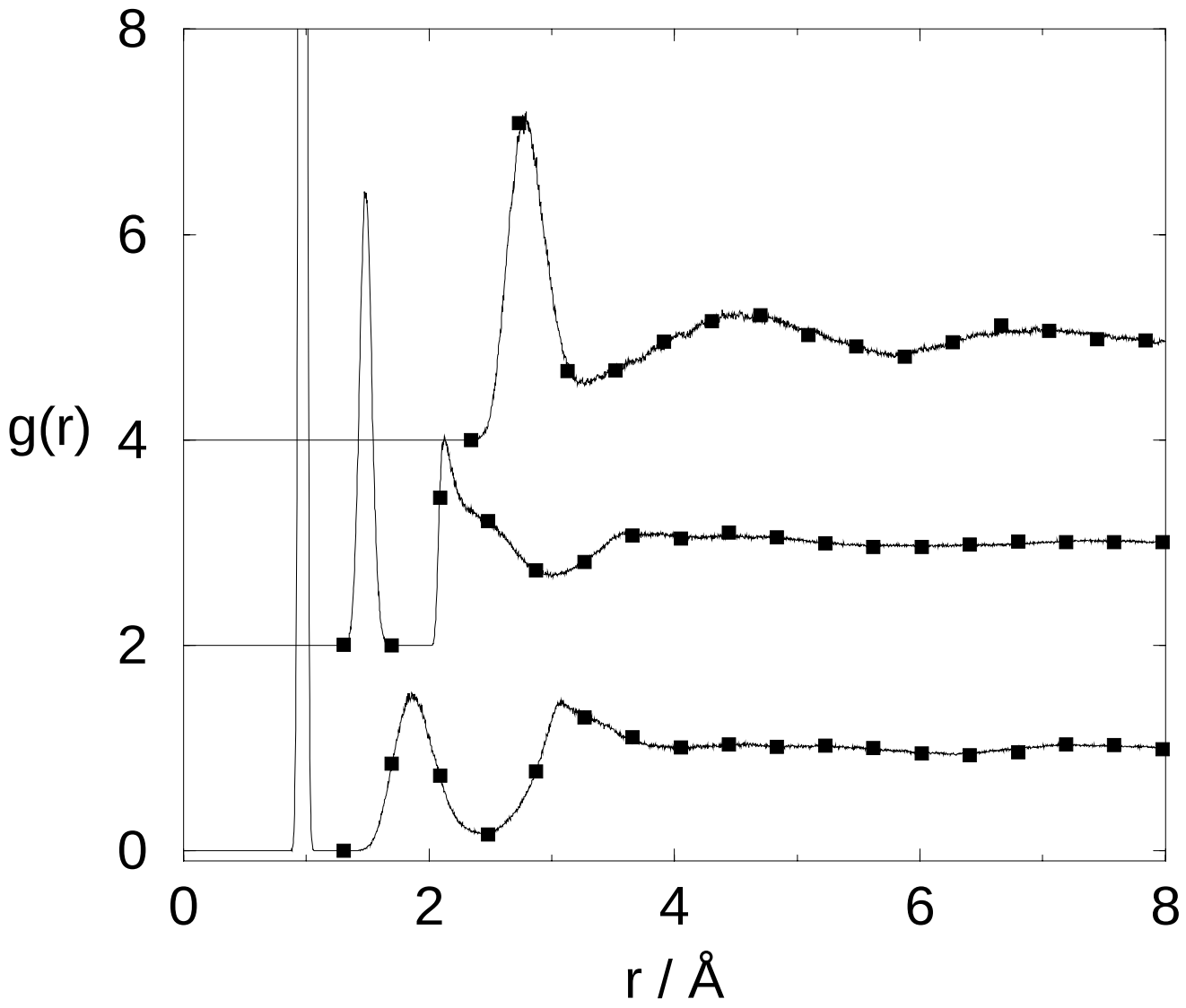
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