

First Principles Molecular Dynamics Simulation of Solution

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We summarize the preliminary results concerning the water-methanol mixture and the DNA electron/proton transfer obtained in this fiscal year using a first principles molecular dynamics method. In the first case, we demonstrated that the shear viscosity of the mixture is reproducible roughly from ~ 100 ps simulations. In the second project, instead, thermal fluctuations are shown to be essential for the spin localization on guanine bases.

Keywords: first principles molecular dynamics, solution, water, methanol, DNA, charge transfer, QM/MM hybrid code

1. Introduction

Although a considerable knowledge of both the physics and the chemistry of aqueous solutions has been accumulated during the years by using various experimental techniques, computer simulations have not yet reached an analogous satisfactory level, mainly because various phenomena occur in aqueous solutions on a much longer time scale than the one affordable with our present computational capabilities. The simulations of radioactive ions in solution are indispensable particularly in the field of nuclear and environmental sciences. A main goal of our joint project is the establishment of simulation techniques enabling us to explore slow processes such as chemical reactions in aqueous solutions with reasonable computational resources. In this fiscal year, besides the development and tuning of the QM/MM hybrid code, we have applied our tuned CPMD code1) to the two open issues, i.e., the water-methanol mixture and the DNA electron/proton transfer. Our preliminary results obtained so far are summarized below along with the present status of the development and tuning of the code.

2. Results

2.1. Water-methanol mixture

Binary mixtures of water and amphiphilic solvent have a wide range of industrial applications. The water-alcohol mixtures are the most familiar binary solvents among such mixtures. However, it is well known that water-alcohol mixtures exhibit an anomalous behavior with respect to the properties of the two separate pure components. Whereas thermodynamic properties of water-methanol mixture are

well characterized experimentally, the local structure is still controversial.^{2,3)} In such a situation first principles molecular dynamics simulations can help to describe the microscopic details and therefore it is able to give the complementary information to the experimental measurements. We have performed Car-Parrinello molecular dynamics simulations of water-methanol mixtures with molar ratio of 1.0:0.0 ($x_m = 0.0$), 0.7:0.3 ($x_m = 0.3$), 0.3:0.7 ($x_m = 0.7$), and 0.0:1.0 ($x_m = 1.0$) to investigate the influence of mixing on hydrogen bond network. Then we examined to what extent their macroscopic quantities are reproduced from ~ 100 ps simulations within a Car-Parrinello molecular dynamics approach. We found that the hydrogen bond network in a water-methanol mixture depends substantially on the water-methanol molar ratio x_m ; the number of hydrogen bonds per molecule presents an anomalous increase at $x_m = 0.3$. The close examination of the interplay between hydrogen bonding and induced dipole revealed that the induced molecular dipole of the constituent molecules is highly correlated with the detailed structure of the hydrogen bond network, indicating that a first principles approach where electrons are treated explicitly is compulsory. The shear viscosity η_s of pure methanol and water-methanol mixture at $x_m = 0.7$ was roughly estimated using the Green-Kubo formula:

$$\eta(t) = \frac{V}{k_B T} \int_0^t dt \langle P_{\alpha\beta}(t) P_{\alpha\beta}(0) \rangle \quad (\alpha \neq \beta), \quad \eta_s = \eta(t = \infty)$$

where $\langle \cdot \rangle$ denotes the thermal average and $P_{\alpha\beta}$ is the stress tensor. As shown in Fig. 1 the estimated shear viscosity η_s from our first principles simulations is in good agree-

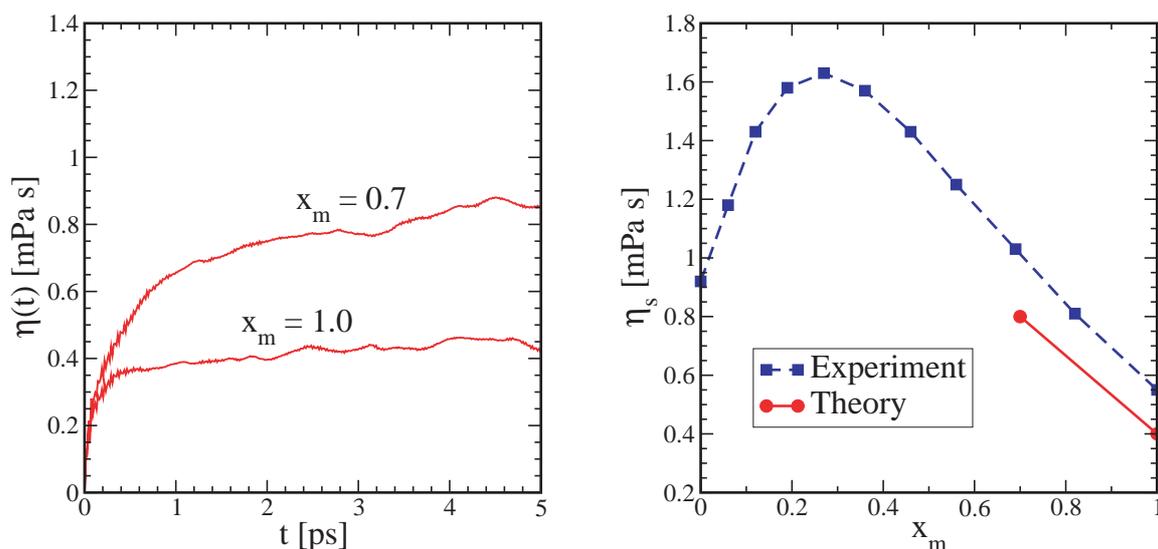


Fig. 1 Viscosity integral of the average stress autocorrelation function as a function of time for pure methanol ($x_m = 1.0$) and water-methanol mixture at $x_m = 0.7$ (left panel). The comparison of the theoretical shear viscosity estimated from first principles simulations with experimental one (right panel).

ment with the experimental one for both the pure methanol and water-methanol mixture at $x_m = 0.7$.

2.2. DNA electron/proton transfer in solution

A DNA radical cation is able to transfer charge via *electron hopping* from a guanine (G) base to the next G-base.⁴⁻⁹⁾ The problem is of wide interest in biology, biophysics and in view of its potential applications in nanotechnology. Nevertheless, the intimate mechanism of the charge transfer (and electron localization) still escapes accurate experimental investigation and several open questions.¹⁰⁾ The simulations performed so far on the ES, within a Car-Parrinello molecular dynamics approach on a hydrated double stranded

G-C DNA dodecamer (Fig. 2) have shown that the spin is generally delocalized on several G-bases. In particular, the strongest localization occurs on those G-bases in which the angle between the vector normal to the plane of the base and the z-axis of DNA is large (Fig. 3, left panel). Thermal fluctuations have been shown to be essential for the spin localization. As a matter of fact, the localization tends to disappear when the temperature is decreased low values (Fig. 3, right panel).

As far as the code is concerned, we could implement a new collective variable¹¹⁾ accounting for the spin density $\rho(\vec{x}) = \rho_{\uparrow} - \rho_{\downarrow}$ and enabling us to control the spin localization and, more generally, electron localization phenomena.¹²⁾

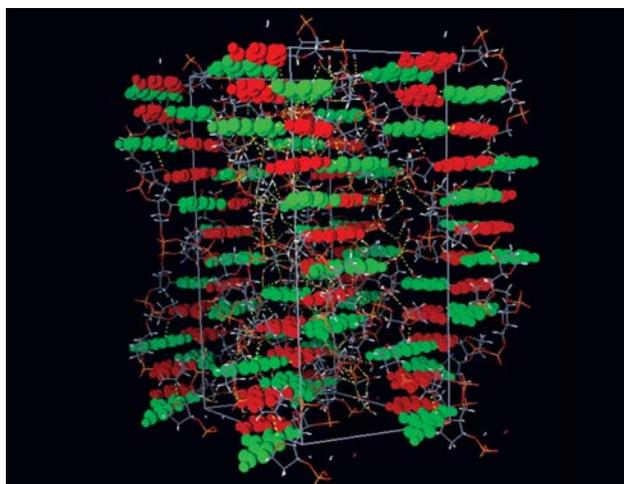


Fig. 2 Double stranded G-C DNA system (G-C dodecamer) used in the simulations with the guanine (G) and cytosine (C) bases shown in green and red, respectively. Other atoms are shown as thin sticks only.

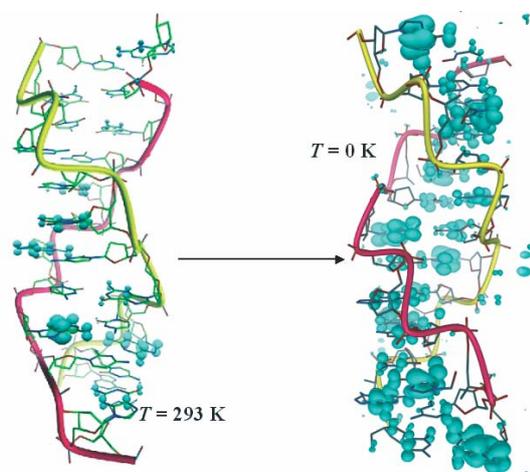


Fig. 3 The DNA poly G-C system at room temperature (left panel) and quenched to about 0 K (right panel). Yellow and purple thick stripes evidence the double helix structure. Light blue clouds are isosurfaces of the spin density distribution along the DNA chain.

This provides a useful tool to explore the reaction paths on the free energy surface. This will be done via a newly introduced metadynamics approach. Finally, we tuned and programmed a Gromos/Amber-like force field and a quantum-classical interface useful to perform hybrid QM/MM calculations, amounting at a reduction in the computational cost and a speed-up in the calculations of large systems. The vector operation ratio of the full quantum code, tuned for ES, is on average 99.421% in the present implementation. The hybrid code, instead, performs with a vector operation ratio between 98.121% and 99.024% depending on the relative size of the quantum and the classical subsystems.

3. Summary

During this fiscal year, we studied the water-methanol mixture and the DNA electron/proton transfer. In the first case, we demonstrated that the shear viscosity of the mixture is reproducible roughly from ~ 100 ps simulations. In the second project, instead, thermal fluctuations are shown to be an essential ingredient to localize the spin on the guanine bases. Both the systems have been fully treated on quantum mechanics grounds. To reduce the computational cost and achieve further speed-up in the calculations of larger systems, a QM/MM hybrid code has been developed and tuned for the ES. Though the performance of our hybrid code is a little bit worse than the standard full quantum code, it already reaches a satisfactory level to use efficiently the ES.

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