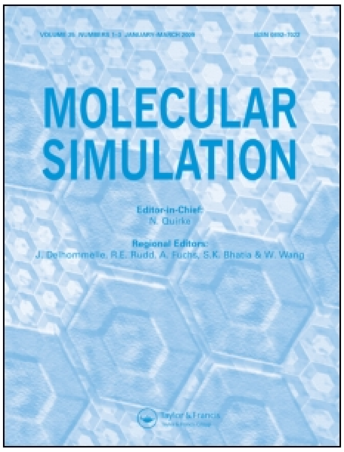

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SOLVATION DYNAMICS FROM NONEQUILIBRIUM MOLECULAR DYNAMICS SIMULATION

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A novel application of the nonequilibrium molecular dynamics method is presented for equilibrium liquids. The colour conductivity algorithm is applied to study solvation dynamics in computer simulations. We characterize ligand exchange reactions by the self-diffusion coefficients of particles in the solvation shell. Comparing this self-diffusion coefficient to that of the pure solvent the kinetic properties of the complex can be estimated. Our studied model is as simple as possible: a solute particle is placed in the origin of the simulation cell surrounded by Lennard-Jones solvent particles. The solute particle interacts with the solvent by pair-wise additive Morse potential. The self-diffusion coefficients are given as functions of solute size and interaction strength expressed in the units of solvent-solvent pair-potential parameters.

KEY WORDS: Nonequilibrium molecular dynamics, colour conductivity, algorithm, solvation dynamics

1. INTRODUCTION

At macroscopic, phenomenological level chemical reactions are followed and described in terms of concentrations. The speed of a reaction is characterized by the reaction rate. The measured reaction rates are usually proportional to the concentrations of the reactants where the coefficient is called the rate constant. In equilibrium, the equilibrium constant of a chemical reaction can be related to the rate constants of the forward and the backward reaction steps. The same equilibrium constant value can be the result of very different reaction rates. This formalism can be used to describe the kinetics of solvation [1].

In liquid phase at microscopic level it is more convenient to characterize the mobility of solvent molecules around the solute by their self-diffusion coefficient [2]. This self-diffusion coefficient should be measured with respect to the position of the solvated particle. Obviously, solvent particles outside of the range of the solvated particle's interaction potential will not be affected in their motion by solvation. Particles in the first solvation shell will change their self-diffusion coefficients the most. The stronger the solute-solvent attraction the more stable the complex. Thus, self-diffusion coefficient of a solvent molecule in the complex characterizes the speed of ligand exchange reactions.

There are several ways of determining self-diffusion coefficients from computer simulations [3]. In equilibrium MD simulations the Green-Kubo form, shown in the following equation, has the advantage that the shape of the velocity autocorrelation function itself contains useful information about the microscopic dynamics of particles.

$$D = 1/3 \int_0^\infty dt \left\langle \frac{\mathbf{p}_i(0)}{m_i} \frac{\mathbf{p}_i(t)}{m_i} \right\rangle \tag{1}$$

An equivalent expression, the so-called Einstein form can easily be derived from (1) assuming that the mean square of distances increases linearly with time [4].

$$D = \frac{1}{6} \lim_{t \to \infty} \frac{\langle \Delta \mathbf{r}^2 \rangle}{t} \tag{2}$$

In dilute solutions the number of ligands is very small compared to the bulk solvent. The contribution of solvate shell particles to D could be negligible. Thus, calculating self-diffusion coefficient for this purpose one should be able to distinguish between the diffusivity of solvation shell particles and that of bulk solvent particles. One should do some sort of book-keeping of solvent particles based on their actual distance from the central solute particle. However, the averages of both (1) and (2) should be calculated for a long time (in principle for infinitely long time) for each solvent particle. During this time at least one of the first shell solvent, i.e. ligand particles leaves the complex. (This is necessary, otherwise there would be no ligand exchange on the time scale of our computer simulation.) *The in and out motion of ligands, however, would prevent the correct book-keeping which is necessary to determine the self-diffusion coefficients of first, second, etc. shell solvents separately.*

To avoid the problems alluded to above we used the colour conductivity NEMD algorithm [4]. It has been proven using linear response theory that the following expression is valid [4]:

$$D = \frac{1}{\beta \rho} \lim_{t \to \infty} \lim_{F_x \to 0} \frac{\langle J_x(t) \rangle}{F_x} \tag{3}$$

where F_x represents the external colour field acting in the x direction and J_x is the generated colour current. The latter is defined as

$$J_x = \frac{1}{V} \sum_{i=1}^{N} c_i \frac{p_{ix}}{m_i} \tag{4}$$

where $c_i = (-1)^i$ is the colour charge which couples to the external field, F_x. The equations of motion are simple modifications of the standard Hamiltonian equations [4].

$$\dot{\mathbf{q}}_i = \frac{\mathbf{p}_i}{m_i}$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i + \mathbf{i} c_i F_x - \alpha \left(\mathbf{p}_i - \mathbf{i} c_i \frac{J_x}{\rho} \right) \tag{5}$$

where $\mathbf{i}$ is a unit vector of the x axis and α is the thermostatting multiplier derived using Gauss' principle of least constraint [4].

An advantage of the colour conductivity algorithm is that contributions to the current can be measured *instantaneously*. The actual position of a solvent particle determines unambiguously the distance of the current source from the solute particle. One should simply choose a reasonable separation from the solute within which a solvent is considered as a ligand. (We think, the first minimum of the pair-correlation function, $g(r)$ is a natural choice.) Now, from the colour current one can determine the value of D for solvate shell molecules separately. A disadvantage of the method is that the equilibrium value can be calculated only from extrapolation. There should be at least two simulations for the same system at different external fields and the limit of (3) should be taken.

2. DETAILS AND RESULTS OF CALCULATIONS

We tested the method on a simple model consisting of 108 Lennard-Jones solvent particles. The state of the system ($T = 0.722$ and $\rho = 0.8442$ in reduced units) corresponded to the triple point of the Lennard-Jones (LJ) liquid. We used a Nosé-Hoover thermostat in (5) to mimic canonical isothermal conditions [3]. The solute particle was "pumped up" in the course of a preliminary run. In fact, this particle was represented by the origin interacting with all the solvent particles through a Morse potential. It is convenient to fix the solute particle because a stronger colour field can move the whole complex when the net colour charge on the ligand particles is not zero.

The Morse potential is more advantageous than the Lennard-Jones form because it has a much shorter range.

$$\varphi_M(r) = A[(\exp(-a(r - r_e)) - 1)^2 - 1] \tag{6}$$

The parameters of (6) were chosen in order to correspond to simple LJ potential values. The size of the solute is determined by r_e, the depth of the attraction by A, and the range of the interaction by a. The latter value was chosen to be 5.6601 for all cases. A was given as a simple number in the units of ε of the LJ potential, namely, 0.5, 1.0, 2.0, 4.0, 8.0, and 16.0. The values of r_e were the following: 0.62, 0.87, and 1.12. Using the latter sizes the neighborhood of the potential minimum for $A = 1.0$ were very close in shape to $\varepsilon = 1.0$ LJ potentials with $\sigma = 0.5$, 0.75, and 1.0, respectively. The 3 independent parameters of the Morse potential made it possible to increase the size of the solute, while keeping the change in the interaction range fairly limited.

We also corrected the density depending on the size of the solute. The actual number densities used were $\rho = 0.8432$, 0.8409, and 0.8365 calculated for the 108 LJ particles. (Obviously, in the thermodynamic limit this should not be done.)

First we determined the self-diffusion coefficient of the pure solvent. This value was 0.031 ± 0.001 in reduced units in accordance with previous results [5]. It should be mentioned that in molecular dynamics ensembles the rhs of Equation (3) is multiplied by $(N - 1)/N$ because the total momentum of the system is conserved [4]. After placing the solute particle in the origin the momentum conservation of solvent particles is no longer valid, so this correction should be omitted.

The overall impact of the solvation can be characterized by the difference in colour flux caused by the presence of the solute. Unfortunately, the larger the system the more difficult to measure it, in particular, if the solute isn't very different from the solvent. The fluctuations in current require very long runs to determine such data accurately.

Thus, we report only self-diffusion coefficients determined by the current of ligand particles.

In a preliminary run we determined the minimum of the pair-correlation function, $g(r)$, around the solute molecule. The place of the minimum was used as the geometric boundary of the first solvate shell. Particles closer to the solute than this R_m value were considered as ligands. Each run consisted of 500 000 timesteps, Δt, which was 0.004 in reduced units and a fifth order Gear algorithm integrated the equations of motion. Long runs were necessary because of the poor statistics of the first shell region. F_x was chosen to be 0.5 and 1.0. We experienced in pilot calculations that for these values the external force dependence was close to linear.

The results are shown in Table 1. A and σ are characterizing the interaction of the solute with solvent particles. (See above for details.) D is the zero field self-diffusion coefficient of ligand particles. These particles were closer than R_m to the solute. n is the average number of ligands for that solute size and interaction strength, i.e. σ and A. Everything is given in reduced units, namely the solvent-solvent Lennard-Jones potential corresponds to $4\{(1/r)^{12} - (1/r)^6\}$. The errors in D values are changing from ± 0.003 to ± 0.002 as one moves towards smaller self-diffusion coefficients. The error in R_m is ± 0.02 which can cause larger uncertainties in the number of ligands for weak solute-solvent interactions. In order to check the errors we calculated D for $R_m - 0.2$ and $R_m + 0.2$ boundary values too. D determined for R_m was always between the self-diffusion coefficients of the smaller and larger shell sizes. Nevertheless, the latter method proved that the results are sensitive for the choice of R_m, therefore other definitions of the solvate shell might also be used to study this problem. (One can number the ligands in terms of their separation from the solute, for instance, and D can be determined for each such neighbor.)

As it can be seen from the table the mobility of ligands changes dramatically in terms of A. For the first two A values it is easier to leave the complex than to move away from an other solvent particle. This is the case for $A = 1.0$ too. Taking into account that the applied Morse potential is shorter ranged than its LJ counterpart with the same depth and shape around its minimum, this is not surprising. The overall impact of increasing solute-solvent attraction is that the number of solvate shell particles increases. In terms of $g(r)$ this is manifested in two tendencies. At one hand the adjacent neighbors are

Table 1 Results of Simulations in Reduced Units

Solute size		*Solute-solvent interaction strength* (*A*)					
		0.5	1.0	2.0	4.0	8.0	16.0
	D	0.033	0.037	0.021	0.021	0.009	0.004
$\sigma = 0.50$	n	5.9	5.9	6.0	6.1	6.2	7.0
	R_m	1.11	1.11	1.06	0.97	0.97	1.00
	D	0.033	0.036	0.030	0.022	0.011	0.006
$\sigma = 0.75$	n	9.2	9.5	9.8	10.2	10.8	11.3
	R_m	1.28	1.28	1.24	1.27	1.22	1.16
	D	0.038	0.034	0.029	0.020	0.010	0.004
$\sigma = 1.00$	n	14.9	15.1	15.6	16.3	17.5	18.5
	R_m	1.54	1.54	1.51	1.54	1.46	1.41

getting fixed more tightly to the minimum of the solute-solvent pair-potential, while even farther neighbors are trying to enter the solvate shell. The first effect decreases R_m, while the second increases it. Depending on the solute-solvent size ratio these two effects cause nonmonotonic change of the first minimum of $g(r)$, R_m, in terms of different packing possibilities.

The same dependence on packing effects might be responsible for the different behaviour of D in the columns of the table. For instance, in the first column D increases with the solute size, while the opposite is true in the next column where $A = 1.0$. Nevertheless, the relatively large errors, in particular, in the case of strong solute-solvent interactions prevent us from drawing very definite conclusions.

The relationship $D \approx \exp(\varphi_M/kT)$ is roughly valid, although it is impossible to verify the differences from that rule accurately, again as a result of the relatively large uncertainties in the small D values.

3. CONCLUSIONS

We presented results of simple model calculations using the NEMD algorithm of colour conductivity to study the kinetics of ligand exchange reactions in a dilute solution where there is no solute-solute interaction. We think, that at present this is the only simple and *principally correct* way to determine the mobility of ligands relative to the position of the solute. We calculated the self-diffusion coefficients of solvent particles being in the first coordination shell of the solute. The self-diffusion coefficient was determined as a function of solute size and solute-solvent interaction strength in terms of the solvent-solvent interaction parameters. The results obtained for this simple system can serve as reference for more realistic cases.

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