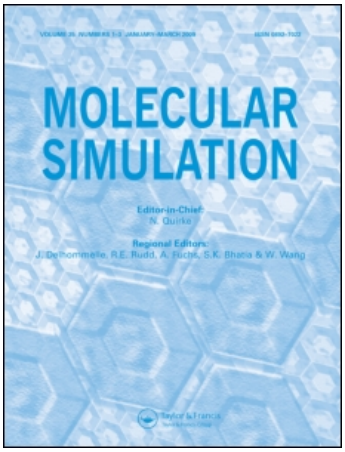

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Solvent Effects on the Shape of a Tetramer

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To cite this Article Padilla, P. and Toxvaerd, S.(1988) 'Solvent Effects on the Shape of a Tetramer', Molecular Simulation, 1: 6, 399 — 402
To link to this Article: DOI: 10.1080/08927028808080961
URL: http://dx.doi.org/10.1080/08927028808080961

Molecular Simulation, 1988, Vol. 1, pp. 399–402
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PRELIMINARY COMMUNICATION

SOLVENT EFFECTS ON THE SHAPE OF A TETRAMER

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(Received February, 1988; in final form April 1988)

The solvent effect on the shape of a tetramer with increasing temperature is analyzed. For this purpose models of an isolated chain and a chain immersed in a solvent have been simulated by Molecular Dynamics. A solvent model represented by stochastic forces has been tested against molecular dynamics results. The behaviour of the mean-square end-to-end distance $\langle R^2 \rangle$ and $\langle I_1^3/S^2 \rangle$ with increasing temperature are shown, where I_1 is the longest eigenvalue of the moment of inertia tensor and S is the radius of gyration. All the chain models studied show different behaviour of these quantities at low temperature compared to high temperature where the shape of the tetramer is temperature insensitive. The main solvent effect is to pospone the transition to higher temperature. The stochastic solvent model qualitatively agrees with molecular dynamics results.

KEY WORDS: Solvent effect, tetramer, shape

The purpose of this preliminary communication is to analyze the solvent effect on the conformation of a chain molecule in a dilute solution with increasing temperature. Earlier investigations [1, 2] show that this solvent effect can be taken into account qualitatively if the dynamics of the system is represented by the Langevin equation. The movement of a particle described by Langevin equation is due to randomly fluctuating forces, which are caused by the deviation of the real force from the mean force exerted by the solvent, and a frictional term proportional to the particle velocity which represents the damping by the solvent. When the assumption of a time independent frictional coefficient is too crude, the dynamical description of the system can be improved by introducing a time dependent frictional coefficient. The corresponding integrodifferential equation is named the generalized Langevin equation [3]. One purpose of the present investigation is to analyze to what extent the solvent effect can be qualitatively obtained from stochastic forces. For this purpose we have studied three systems: an isolated chain molecule and two models for the fluid solution of the same chain molecule. The first fluid solution system is studied using a Molecular Dynamics simulation. For the second the solvent effect is described by a stochastic

model where the dynamics of the chain molecule is obtained by solving the generalized Langevin equation as described in reference [4].

The chain molecule is a tetramer where any two beads along the chain interact via Lennard-Jones (LJ) potentials plus a harmonic potential between neighbour beads. Energy and length units are given by the two LJ-parameters ε and σ and the harmonic potential constant is set equal to 20. The chain molecule is immersed in a solvent of simple particles which only interact (solvent-solvent, solvent-beads) via repulsive LJ-potentials. The time evolution of the tetramer is calculated by molecular dynamics and by solving the generalized Langevin equation,

$$m\,d\mathbf{v}_i/dt = -m\int_0^t dt'\,M_i(t-t')\mathbf{v}_i(t') + \mathbf{r}_i(t) + \mathbf{e}_i(t) \tag{1}$$

for the i'th bead with mass m, velocity $\mathbf{v}_i(t)$ and intramolecular force $\mathbf{e}_i(t)$. The stochastic solvent force $\mathbf{r}_i(t)$ is obtained from the memory function $M_i(t)$ (fluctuation-disipation relation). Most of the solvent friction/force on a bead arises from its interactions with the neighbouring solvent particles in the cage surrounding a subunit. This short-time/short-range behaviour is excellently described by a Gaussian memory function [5, 6],

$$M(t) = K_1 \exp(-K_2 t^2/2) \tag{2}$$

where the two parameters K_1 and K_2 can be determined by molecular dynamics from

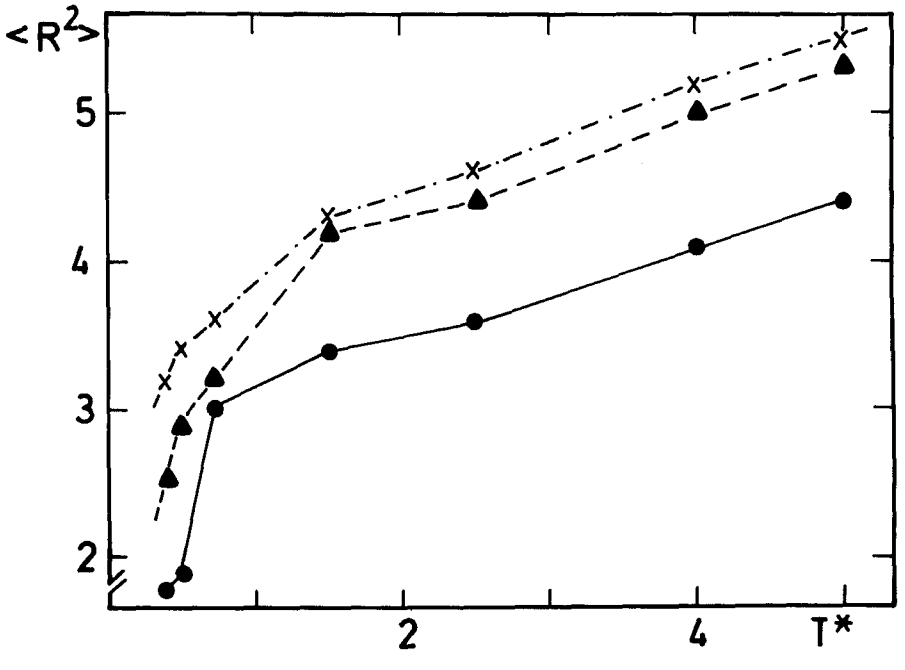

Figure 1 Mean-square end-to-end distance $\langle R^2 \rangle$ as solvent a function of the reduced temperature $T^* = kT/\varepsilon$. The points are for: a tetramer in a molecular dynamics (●), generalized Langevin equation (▲) and free tetramer (×), respectively.

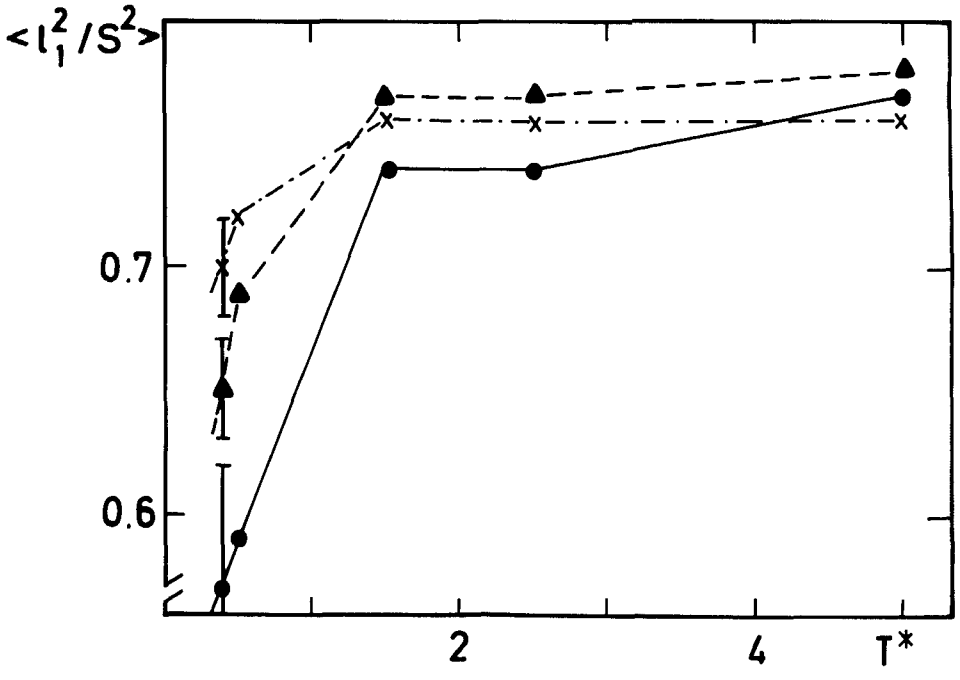

Figure 2 The asphericity ratio of the tetramer as a function of temperature, given by the mean-square of the ratio between the longest axis l_1 of the chain and the ratio of gyration S. Signature is as in Figure 1.

the force moments of the solvent. For this reason, the solvent is modelled by particles which only interact through short-ranged potentials. The calculations were performed at the fluid density $\varrho\sigma^3 = 0.75$ and the values of K_1 and K_2 are obtained (by interpolation) from reference [6]. The solutions of the generalized Langevin equation is compared with corresponding molecular dynamics calculations of a free tetramer and a tetramer immersed in 212 solvent particles.

The equilibrium quantities in which we are interested are the mean-square end-to-end distance, $\langle R^2 \rangle$, the mean square of the radius of gyration $\langle S^2 \rangle$ and $\langle l_1^2/S^2 \rangle$, $\langle l_2^2/S^2 \rangle$ and $\langle l_3^2/S^2 \rangle$ where l_1, l_2, l_3 are the three eigenvalues of the moment of inertia tensor. The means are obtained by averaging over of the order 10^5 timestep ($\sim 10^{-9}$ s) for the generalized Langevin equation and the free tetramer and 6 10^4 time steps ($\sim 10^{-10}$ s) for the fluid molecular dynamics system.

The results are shown in Figure 1 and Figure 2. They display a different behaviour at low and high temperatures. At low temperatures the attractive intramolecular interactions ensure a compact mean conformation corresponding to low values for $\langle R^2 \rangle$. When the temperature is increased the system shows a transition into more open mean conformations. The mean-square end-to-end distance, as well as the other mean values show a weak linear dependence with the temperature above the transition zone $T^* \sim 0.5 - 1$. The fluid molecular dynamics system (●) deviates systematically from the free tetramer (×) and the stochastic solvent model (▲) by having a shorter value for $\langle R^2 \rangle$. In this same temperature range, however, the shapes are almost the same for the three models and temperature insensitive. This can be seen from Figure 2 which shows the mean-square of the ratio of the longest axis, l_1 and S, as a function

of the temperature. Corresponding graphs of $\langle l_2^2/S^2 \rangle$ and $\langle l_3^2/S^2 \rangle$ exhibit the same behaviour. So the systematic deviation in $\langle R^2 \rangle$ is only caused by a shorter mean bond length in the (constant density) fluid molecular dynamics system, which is kept at a high pressure by the periodical boundaries, whereas the free polymer and the stochastic solvent model are both for a system at zero pressure, and this results in a slightly longer mean bond length. But these differences in the mean bond lengths do not change the shape of the tetramer above the transition temperature.

The solvent effect is given by the differences between fluid molecular dynamics system (●) and the free tetramer (×) and its effect is mainly that it postpones the transition to a higher temperature. The stochastic model has the same qualitatively effect, but the transition takes place at a lower temperature than in molecular dynamics solvent. This shortcoming in the generalized Langevin equation may be specific for the present model, caused by the longer mean bond length, since a longer bond length implies weaker attractive bead-bead forces. But this shortcoming can also come from the assumption of isotropic friction, independent of the tetramer configuration. It could be that it is still too crude an approximation to describe the behaviour of the chain molecule at low temperatures.

We can conclude that at high temperature the solvent does not have any significant effect on the mean conformation of the chain molecule. But at low temperature the interplay between the interactions of chain segments among themselves and with the solvent determines the transition zone, so any model representing the solvent effect on the chain needs to be tested at low temperature.

A grant for computer time by the Danish Natural Research Council is gratefully acknowledge.

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