

# **Multi-Scale modeling of Diffusion of gases in polymer**

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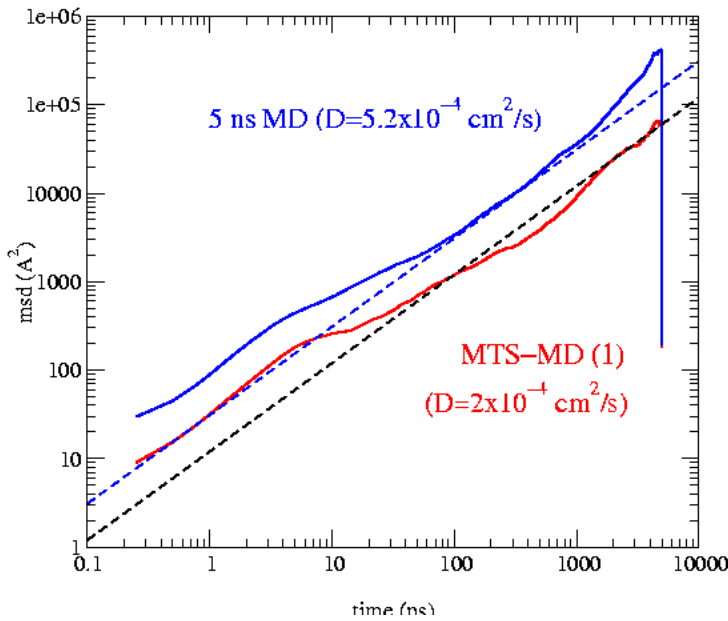
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Atomistic modeling of gas diffusion in polymers is a challenging problem because of the long the time-scales (from tens of nanoseconds up to microseconds) required to achieve the Fickian, asymptotic, regime [linear relation between the mean square displacement (MSD) of the penetrant molecule and time]. Such long time-scales make Molecular Dynamics simulations inappropriate. We make use of the fact that the high frequency and short wave-length modes of the polymer don't play an important role in the diffusion process to devise a computationally efficient approach [named Multiple Time Step Molecular Dynamics (MTS-MD)] that allows us to reach the long time-scales involved.

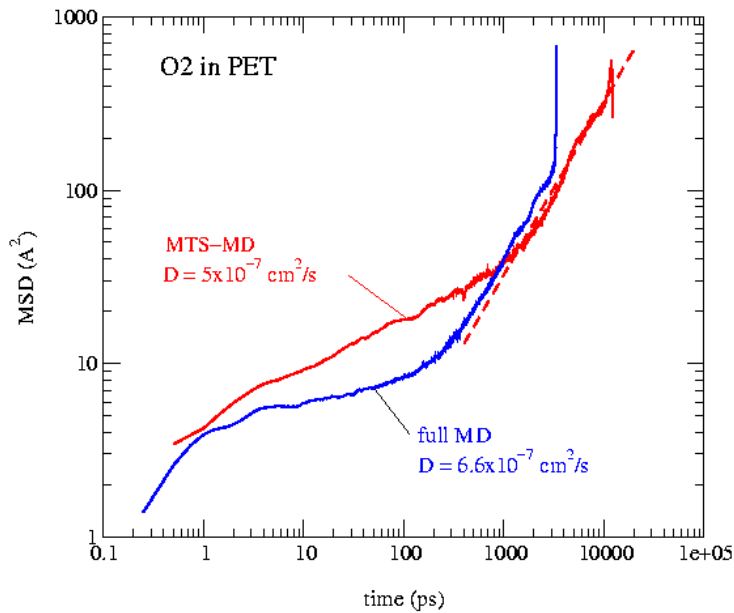
The MTS-MD approach consists of performing a series of short (typically 0.5 ps) MD run allowing the motion of the gas molecule in a fixed polymer matrix. After each MD run the positions of the atoms forming the polymer are updated and the gas molecule continues its motion experiencing all the molecular interactions with its surrounding medium; this procedure is repeated until the desired simulation time is achieved. The frames of the polymer are obtained from a previously done MD run of the matrix with no penetrant molecule; in this way we capture the thermal fluctuation and time correlations critical for the diffusional process. The MD run of the polymer does not need to be very long since the same frames can be used several times; we find that a 200 ps MD run of the polymer is sufficient to study diffusion. This approach is computationally very fast and efficient since only the motion of the diffusing molecule needs to be solved; the dynamics of the polymer need to be computed only once and for a short time.

In order to test the new approach we compare the MTS-MD results with regular Molecular Dynamics (MD) simulations. We performed a 5 ns long full MD run of helium in PET at T=600 K. The blue line in Figure 1 shows the mean square displacement (MSD) of the He atom as a function of time, the calculated diffusion constant is  $5.2 \times 10^{-4}$



**Figure 0 Diffusion of He in PET.**

the full MD results ( $D=6.6 \times 10^{-7} \text{ cm}^2/\text{s}$ ). Slightly lower diffusion constants are expected in



**Figure 2 O2 diffusion in PET at**

$\text{cm}^2/\text{s}$ . The red line in Figure 1 represents the MTS-MD result leading to a diffusion constant of  $\sim 2 \times 10^{-4} \text{ cm}^2/\text{s}$  in good agreement with the full MD result.

In Figure 2 we show a comparison of full MD and the MTS-MD approach for  $\text{O}_2$  diffusing in PET at  $T=300 \text{ K}$ . The diffusion constants obtained using the MTS-MD approach is in very good agreement with

the MTS-MD approach since the polymer is not allowed to relax in the presence of the diffusing molecule, thus overestimating the energy barriers the gas has to overcome in order to move. The MTS-MD approach allows us to bridge the time-scales and perform atomistic simulations of the slow process of gas diffusion in polymers in an efficient way.

