1. Introduction
In this work we report on the improvement of a novel method developed by us for detecting the so-called diffusion "jumps" of small molecules through polymers. Such jumps are observed in the course of Molecular Dynamics (MD) simulations and are believed to constitute one of the main mechanisms underlying mass transport processes in amorphous matter.

Our method is placed in the context of a more general study conducted by us, about the dependence of diffusion processes on the characteristics of various molecular systems and conditions imposed. A brief account of our findings is also provided.

4. Jumps and translational diffusion
Overall translational diffusion, quantified in the form of self-diffusion coefficient, \( D_s \), which we compute by means of the Einstein relation:

\[
D_s = \lim_{t \to \infty} \frac{1}{2t} \langle \| r(t + \tau) - r(t) \| \rangle,
\]

is the result of more than one microscopic mechanisms (jumps, smooth translation etc). The average jump length and a corresponding frequency \( \nu \), serve to define a jump induced diffusion,

\[
D_{s,jump} = \sum_i \nu_i \langle \lambda_i (\Delta t) \rangle \quad \text{or} \quad \nu = \langle \lambda \rangle_i,
\]

which in turn, is a measure of the jumps mechanism contribution to the total diffusion observed.

It has been argued that diffusive jumps in polymer matrices constitute rare events, even in the liquid state, so that their statistical treatment in the framework of molecular simulation is meaningless.

Plots of the \( R_G \) curves reveal frequent occurrence of "attempted" diffusive jump events. Their weighted counterparts on the other hand, indicate that most of them are unsuccessful, as the small ratio of the weighted over unweighted values, clearly shows. This is an evidence of the penetrant molecules being trapped in their host cavities for long time scales.

Thus, diffusive jumps appear to have a small contribution to the overall diffusion observed in the course of our simulations. The penetrants transport process is a more complicated one, and more than one mechanisms should be present (e.g. smooth particle translation through the matrix thanks to the latter's fluctuations, or motion imposed by the polymer itself, which pushes the particles from one region to another).

Finally, it is worth noting that the incorporation of the weighting factor, as discussed in section 3, leads to an asymptotically constant value of diffusive jump size. This has been proven theoretically and simulations performed thus far, offered substantial supporting evidence (Fig. 4).

Reference:

About simulation details:

5. Application
The method has been successfully tested in systems of normal alkanes, \( C_nH_{2n+2} \) for \( n = 10 \) and 20 and gaseous alkanes dispersed therein. It was shown that jumps are clearly not the only diffusion mechanism present.

In the present work we extend our study to polymer resembling matrices, with \( n = 100 \) and 200 and methane or n-butane dispersed therein.

7. Results and discussion

6. Simulation Stages and Details
• Construct amorphous United Atom polymeric matrix with proper torsion angle distribution.
• Optimize initial configuration using Monte-Carlo sampling at fixed density.
• Evolve in time (Molecular Dynamics) employing Gear Predictor-Corrector integration scheme.
• NPT ensemble (Nosé-Klein method), 1 at, 450 K. Time simulated, 6 ns, the first 1 ns used for equilibration.
• Integration time-step, 1 fs.
• Force-Field based on a TraPPE variation allowing bond substitution for varying species with same parameters.
• Number of polymer atoms fixed at 1000.
• Penetrants number fixed at 20 molecules.

Observations
• Decrease of jumps size (whether weighted or unweighted) follows that of \( D_s \) with degree of polymerization.
• As expected, heavier penetrants are less mobile in terms of their centre of mass displacement in the course of short time scales (of the order of a jump event life span)
• Most "attempted" jump events have a small contribution to the overall diffusion measured in the course of the simulations. Therefore, other microscopic mechanisms are also present.
• Evidence for persistent anisotropy even in Einstein regime.
• Decrease of diffusive jumps average size with polymer molecular weight, similar to that of \( D_s \).