

MECHANISMS OF GASEOUS MOLECULES DIFFUSION THROUGH AMORPHOUS LINEAR POLYMERS: A STUDY VIA MOLECULAR DYNAMICS SIMULATION

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Introduction

In this work we study the main diffusion mechanism of small molecules dispersed in polymeric matrices by means of Molecular Dynamics simulation. Emphasis is given on the identification of so called diffusion "jumps" or "hopping" mechanism. A method is proposed for the quantitative definition and treatment of separate jump events. We also study characteristics of small penetrant motion with respect to both short and long space-time scales. Specifically, we investigate orientational features of diffusive motion in the aforementioned scales.

Diffusion Coefficients

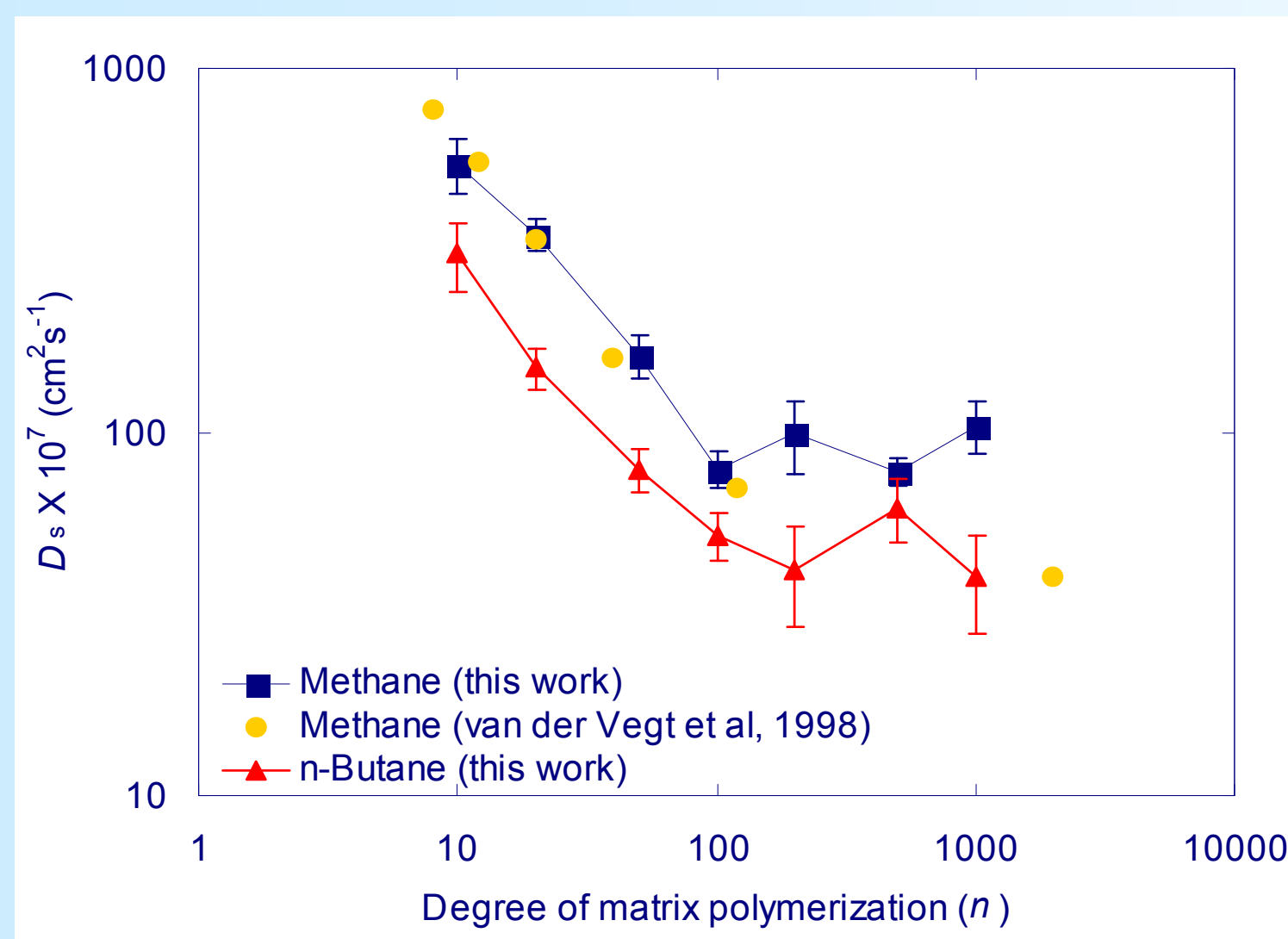


Fig. 1 log-log plot depicting diffusion coefficients obtained for CH₄ and C₄H₁₀ in matrices of varying molecular weight

<i>n</i>	10	20	50	100	200	500	1000
CH ₄	545	348	163	79	99	78	104
C ₄ H ₁₀	310	150	79	52	42	62	40

Other penetrant in C ₁₀₀ H ₂₀₂	CH ₄ (mixed with C ₄ H ₁₀)	C ₄ H ₁₀ (mixed with CH ₄)	C ₂ H ₆	C ₃ H ₈
	137	57	74	50

TABLE 1 D_s ($\times 10^7$ cm² s⁻¹) of small alkane molecules through "polymer" C_{*n*}H_{2*n*+2}, as a function of *n*}

Jumps identification method

Penetrant jumps from one free volume cavity to another is considered as the main mechanism of low molecular weights species diffusion. To verify this, a measure is given in terms of the local radius of gyration R_G

$$R_G(t; \Delta t) = \sqrt{\frac{1}{N} \sum_{i=1}^N (\mathbf{R}_i - \mathbf{R}_{CM})^2}$$

over a set of successive penetrant positions for different values of a time delay Δt , rolling over the species trajectory.

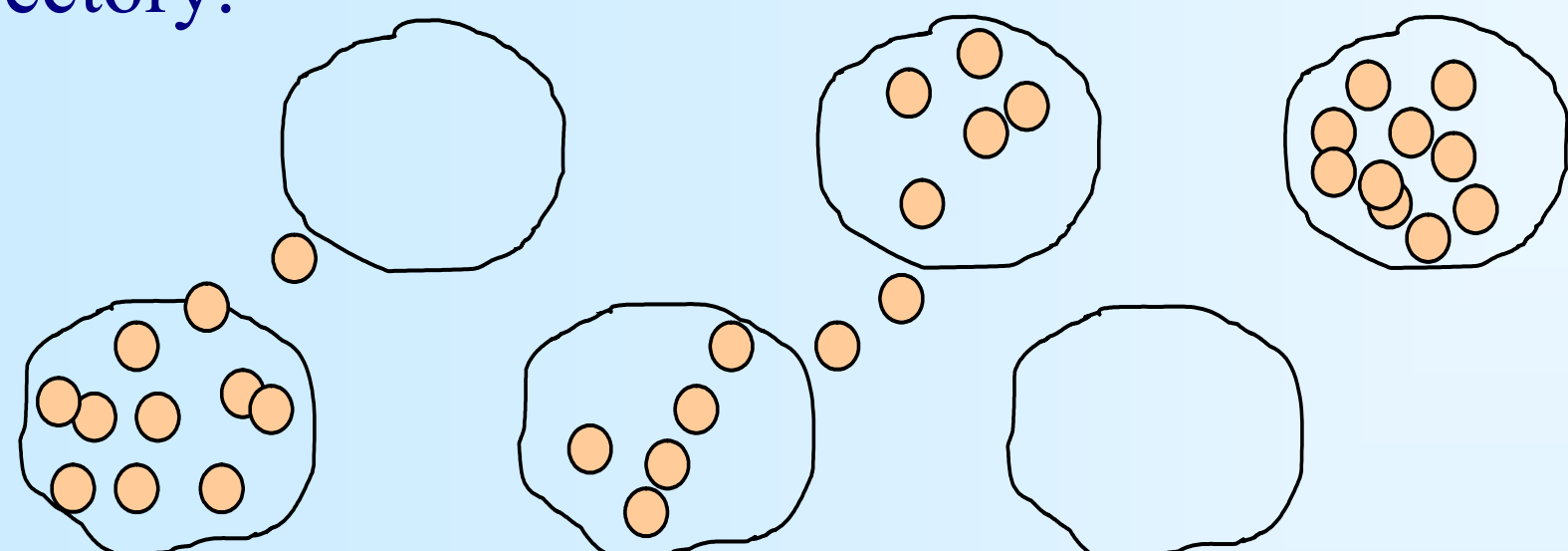


Fig. 4 Schematic depiction of the algorithm. Jump events correspond to elongated distributions of successive trajectory points resulting in a sharp increase of the respective radius of gyration. Different time delays Δt serve to identify the most prominent jump events.

Fig. 7 (on the right) Size of methane and n-butane diffusive jumps for a time delay $\Delta t = 100$ ps, averaged over all penetrants of each kind, with respect to degree of polymerization, *n*, of the C_{*n*}H_{2*n*+2} matrix. A threshold value of $n \approx 100$ is observed, beyond which a constant jump size is established – see also Fig. 1 of diffusion coefficients calculated.}

About simulation details:

- Martin, M. G.; Siepmann, J. I., *J. Phys. Chem. B*, **1998**, 102, 2569 (TraPPE force field)
- Nosé, S.; Klein, M. L., *Mol. Phys.* **1983**, 50, 1055 (NPT ensemble)

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, 293.15 K.
- Time simulated, 6 ns, the first 1 ns used for equilibration.
- Integration time-step, 0.5 fs.
- Force-Field based on a TraPPE variation allowing bond substitution for varying species with same parameters.
- Polymeric matrices chosen from the **normal alkane** family C_{*n*}H_{2*n*+2} for *n* = 10, 20, 50, 100, 200, 500, 1000.}
- Number of polymer atoms fixed at 1000.
- Penetrants number fixed at 20 molecules.
- Additionally, three runs involved methane+butane (10:10) **mixtures** introduced into 100mer matrices.

Anisotropy

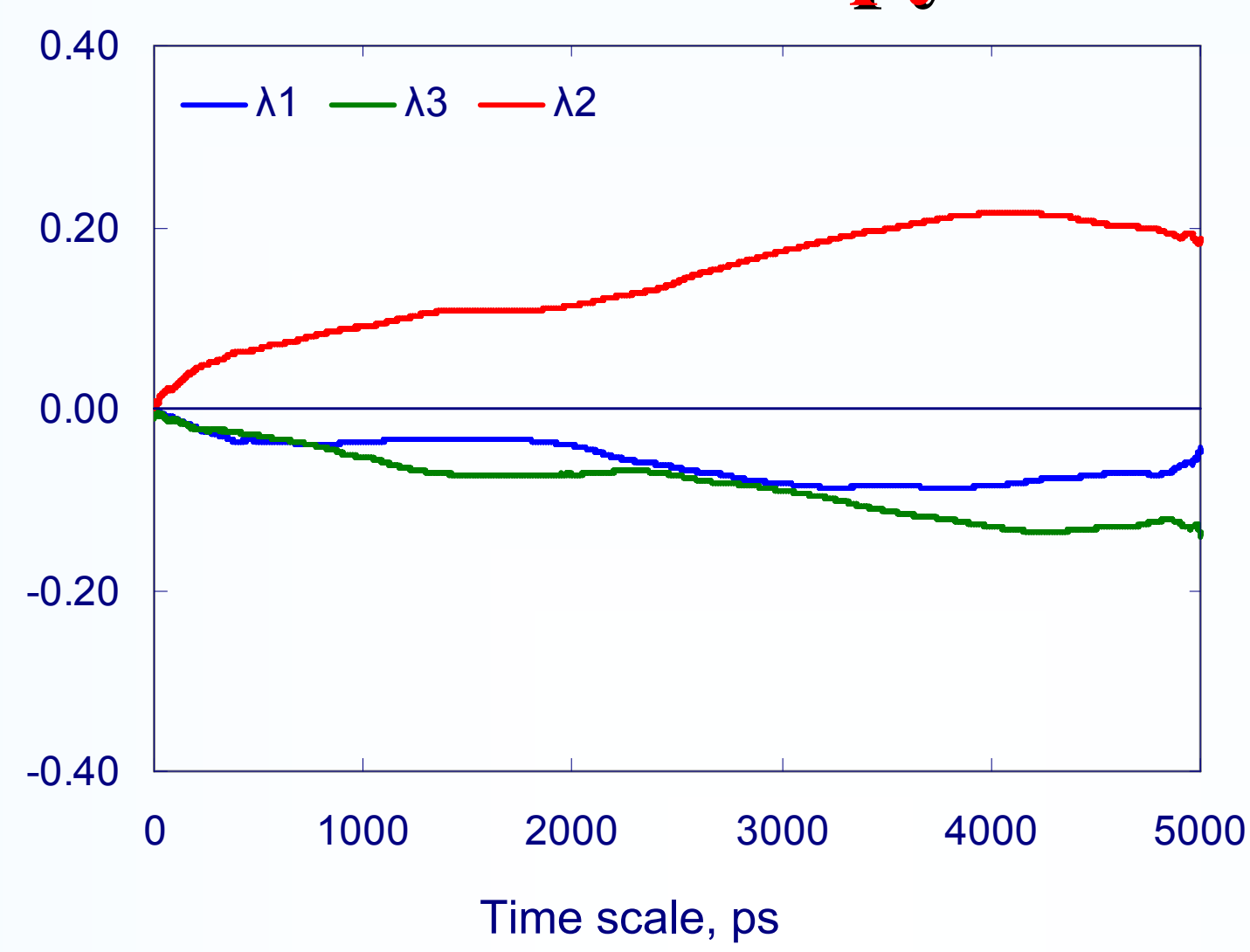


Fig. 2 CH₄ in C₁₀₀₀H₂₀₀₂. Eigenvalues of the displacement matrix (normalized with mean square displacement and shifted by -1/3)

Anisotropy is present *even if mean square displacement exhibits linear dependence on time-scales.*

Methane Jumps

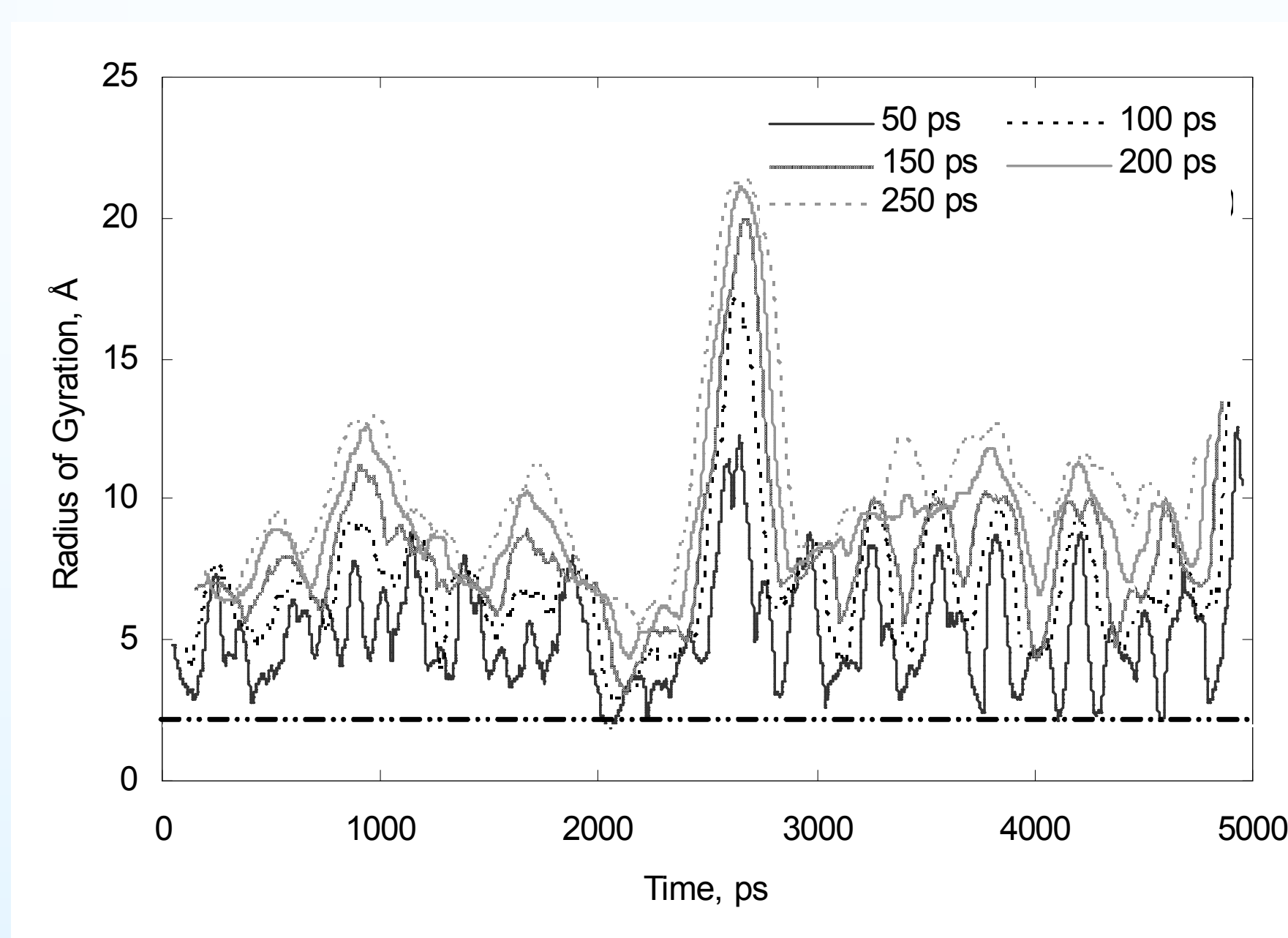
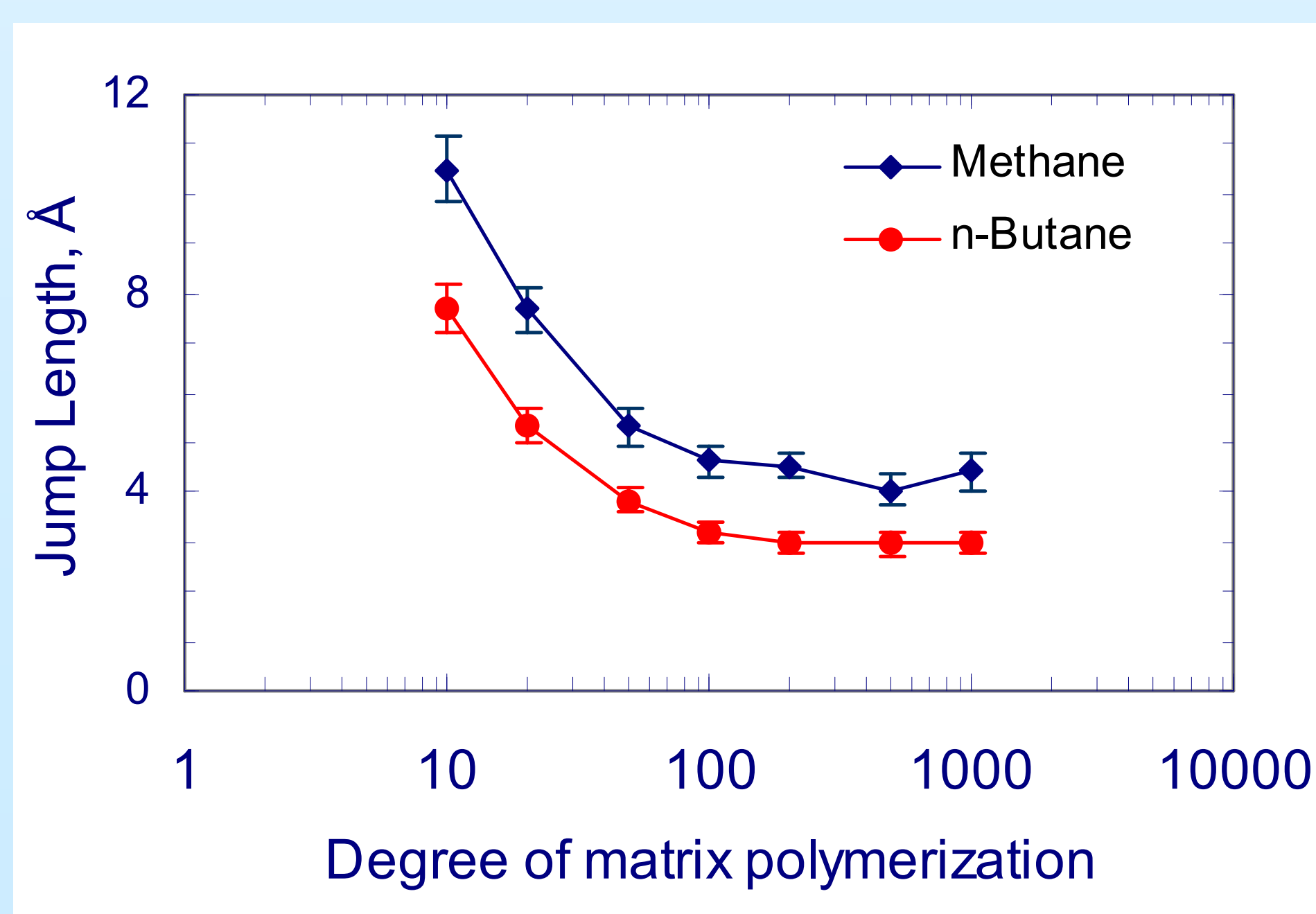


Fig. 5 Jumps of one methane molecule moving through a 100mer matrix are identified as peaks in the plot of R_G versus time. Different time delays Δt serve to identify most prominent events.

Jumps Statistics



Analysis of Results

- **Self-diffusion Coefficients** D_s are obtained by Einstein relation:

$$D_s = \lim_{t \rightarrow \infty} \frac{1}{6t} \left\langle |\mathbf{r}_i(t+t_0) - \mathbf{r}_i(t_0)|^2 \right\rangle_{i,t_0}$$

- Autocorrelation functions of velocity components parallel and perpendicular to penetrant's end-to-end vector computed for ethane, propane and n-butane to investigate aspects of **diffusive motion orientation** at short space-time scales.
- Elements of the displacement correlation matrix $\langle \Delta \alpha \Delta \beta \rangle$ ($\alpha, \beta = x, y, z$) computed to check presence of **anisotropy** in long space-time scales. Another quantitative descriptor of the anisotropy is given in terms of the three eigenvalues of the correlation matrix.
- A new method is proposed for providing a measure of **diffusive jumps** in terms of the local radius of gyration R_G over a set of successive penetrant positions.

Orientation

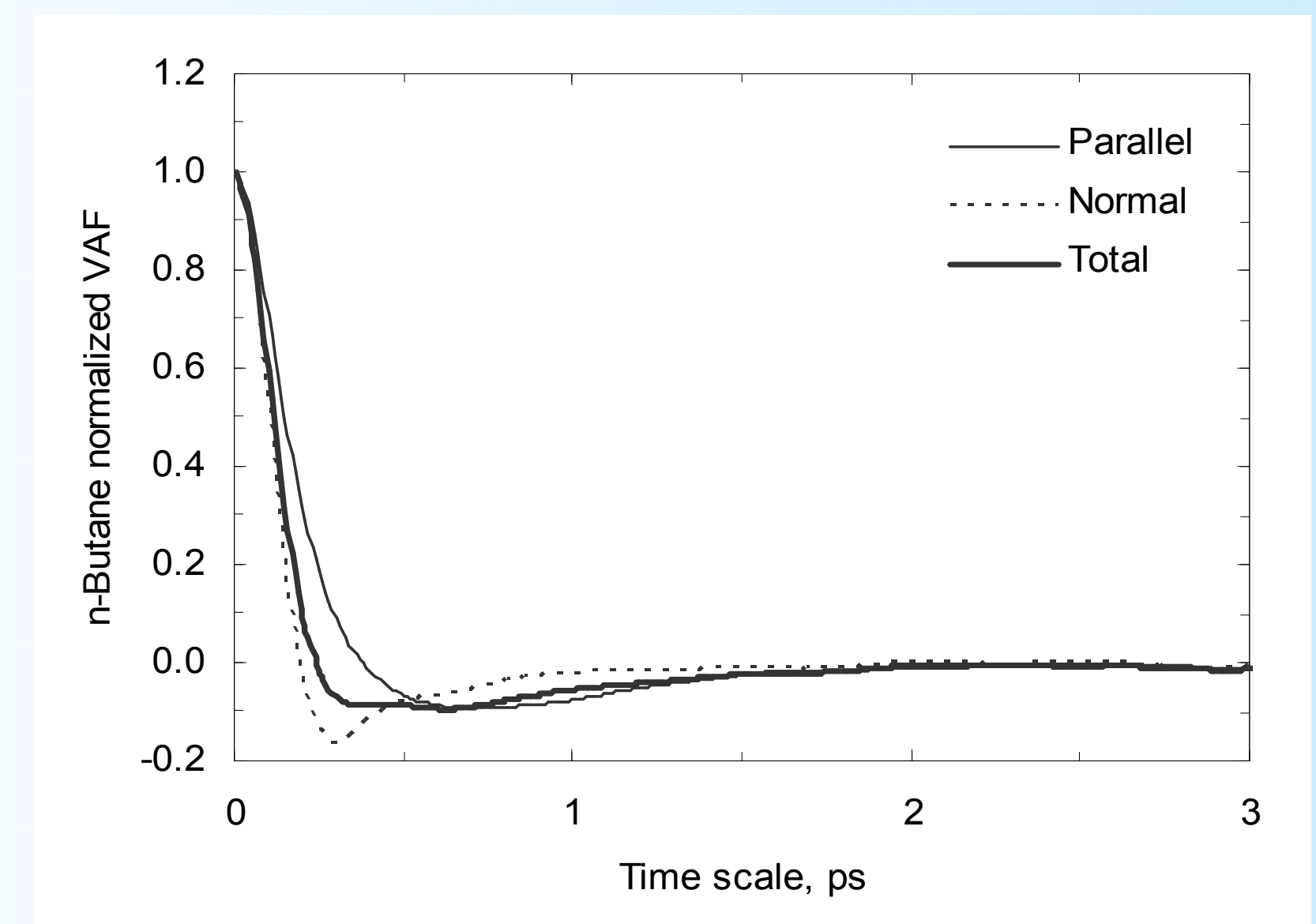


Fig. 3 C₄H₁₀ in C₁₀₀H₂₀₂. Velocity Autocorrelation Functions (VAF) of components parallel and perpendicular to molecular end-to-end vector, together with total VAF

Integration to infinite time scales provides longer correlation times for parallel component, indicating *relatively persistent motion along end-to-end vector*

Butane Jumps

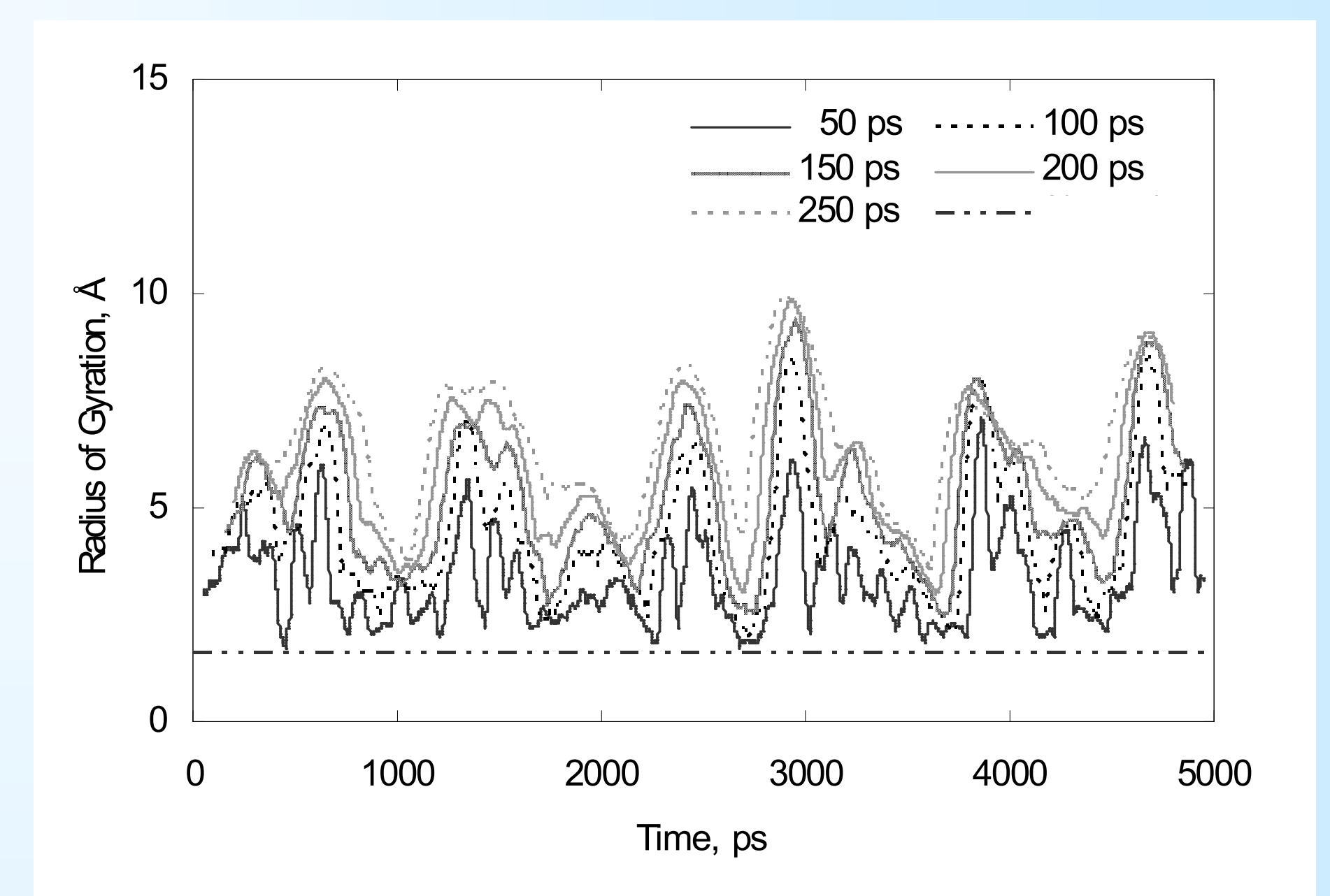


Fig. 6 Same as in Fig. 5 for one n-butane molecule moving through a 100mer matrix. Dotted line in both this and Fig. 5 correspond to penetration length $\xi = (D_s \Delta t)^{1/2}$ for $\Delta t = 50$ ps

Observations

- Decrease of D_s with degree of polymerization until an asymptotic value is reached.
- Increase of CH₄ diffusivity when C₄H₁₀ is also present
- Linear penetrants prefer to move along their end-to-end vector.
- Evidence for persistent anisotropy even in Einstein regime.
- Decrease of diffusive jumps average size with polymer molecular weight, similar to that of D_s .