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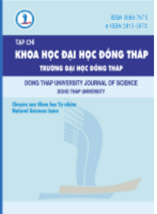

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A NOVEL APPROACH TO PREDICTING STRUCTURAL RELAXATION IN POLY(ETHYLENE OXIDE)

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Abstract

Poly(ethylene oxide) (PEO) has emerged as a critical polymer for biomedical and energy applications due to its unique combination of biocompatibility, chain flexibility, and exceptional ion solvation properties. The glass transition temperature (T_g) serves as a fundamental parameter controlling PEO's segmental dynamics, ionic conductivity, and mechanical behavior which are crucial for its functional performance. Molecular dynamics (MD) simulations are employed to systematically investigate the T_g value of PEO and provide atomistic insights into its thermal transitions and dynamic properties. Then, the MD-predicted T_g is integrated into the Elastically Collective Nonlinear Langevin Equation (ECNLE) theory to determine the temperature dependence of structural relaxation time ($\tau_\alpha(T)$) and diffusion processes. The theoretical calculations obtained quantitatively agree with previous experimental data.

Keywords: Diffusion, glass transition temperature, PEO, poly(ethylene oxide), relaxation time.

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PHƯƠNG PHÁP MỚI DỰ ĐOÁN QUÁ TRÌNH TÁI CẤU TRÚC PHÂN TỬ TRONG POLY(ETHYLENE OXIDE)

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Tóm tắt

Poly(ethylene oxide) (PEO) là một loại polyme quan trọng cho các ứng dụng y sinh và năng lượng do sự kết hợp độc đáo giữa tính tương thích sinh học, tính linh hoạt của chuỗi và các đặc tính hòa tan ion đặc biệt. Nhiệt độ chuyển thủy tinh (T_g) đóng vai trò là thông số cơ bản kiểm soát động lực học phân tử, độ dẫn ion và tính chất cơ học của PEO, tất cả tính chất này đều rất quan trọng đối với hiệu năng hoạt động của vật liệu. Chúng tôi sử dụng mô phỏng động lực học phân tử (MD) để nghiên cứu một cách có hệ thống giá trị T_g của PEO và cung cấp những hiểu biết về nguyên tử vào các quá trình chuyển đổi nhiệt và đặc tính động của nó. Sau đó, giá trị T_g được dự đoán bởi mô phỏng MD sẽ được tích hợp vào lý thuyết Phương trình Langevin phi tuyến tính tập thể đàn hồi (ECNLE) để xác định sự phụ thuộc của thời gian tái cấu trúc $(\tau_\alpha(T))$ và các quá trình khuếch tán vào nhiệt độ. Các kết quả tính toán lý thuyết của chúng tôi hoàn toàn phù hợp với dữ liệu thực nghiệm trước đây.

Từ khóa: Khuếch tán, nhiệt chuyển pha thủy tinh, PEO, poly(ethylene oxide), thời gian tái cấu trúc.

1. Introduction

Poly(ethylene oxide) is a synthetic polymer with exceptional physicochemical properties. Thus, it has become one of the most versatile materials in modern technology (Liechty et al., 2010; Xue et al., 2015). Its water solubility, biocompatibility, and high chain flexibility have enabled broad applications in such fields as biomedical engineering, pharmaceuticals, and energy storage technologies.

In the pharmaceutical industry, PEO has been widely employed as an excipient in drug delivery systems to enhance drug solubility and regulate release kinetics. Thus, it has been exploited in matrix tablets, hydrogels, and micellar formulations. Additionally, its non-toxic nature and protein-resistant properties have facilitated applications in biomedicals, including tissue engineering scaffolds and surface coatings for medical devices (Liechty et al., 2010). Beyond biomedical uses, PEO has drawn considerable interest in energy storage, particularly as a solid polymer electrolyte in lithium-ion batteries, where its ether-oxygen moieties effectively solubilize lithium salts and enable ion transport (Mindemark et al., 2018).

A fundamental factor governing PEO's performance across these applications is its glass transition temperature. This critical thermal parameter, typically between 211 K and 226 K for high molecular weight PEO, defines the transition between the glassy and rubbery states (Faucher et al., 1966; Lunkenheimer et al., 2025; Schmidt et al., 1998; Vrandečić et al., 2010) and estimates molecular dynamics of amorphous materials. In solid polymer electrolyte systems, T_g is a key determinant of ionic conductivity to facilitate ion diffusion as the segmental motion of polymer chains becomes activated above T_g. Below T_g, PEO exists in a rigid and glassy state with restricted chain mobility which significantly impairs ion transport. Consequently, optimizing T_g has become a central focus in developing high-performance polymer electrolytes for next-generation energy storage.

Many approaches could be used to determine the glass transition temperature of polymers. Differential Scanning Calorimetry (DSC) is one of the most common techniques but often suffers from overlap between the glass transition and melting endotherms (Wunderlich, 2005). Dynamic Mechanical Analysis (DMA) provides higher sensitivity to mechanical responses near T_g but requires precise sample preparation and interpretation. Broad dielectric spectroscopy (BDS) offers molecular-level insights into relaxation dynamics but this is very expensive and not a common instrument accessible in developing countries. These experimental limitations have driven interest in theoretical and computational approaches including molecular dynamics (MD) simulations and statistical mechanical models to predict and analyze the glass transition behavior of polymers in general and PEO-based systems in particular.

The ECNLE theory has been recently used and developed to investigate the glassy dynamics of many amorphous materials, including metallic glasses, polymers, drugs, organic materials, and thermal liquids (Miccio et al., 2022; Mirigian et al., 2015; Phan, 2020; Phan et al., 2025, 2018b, 2018a; Phan, Knapik-Kowalczuk, et al., 2019). The theory uses the T_g value as its only input parameter for determining the temperature dependence of structural relaxation time and diffusion constant in bulk (Phan et al., 2025, 2018b) and thin-film (Mirigian et al., 2015; Phan et al., 2018a) systems. The timescale of relaxation calculated using the ECNLE theory spans from 1 ps to 100s, which covers both the MD simulation and experimental timescales. Note that the simulation timescale is less than 10^5 ps. Thus, ECNLE calculations allow for an understanding and prediction of the molecular dynamics of amorphous materials investigated in experiments and simulations.

In this work, we combine, for the first time, MD simulations and the ECNLE theory to investigate the glassy dynamics of PEO. First, we use MD simulations to estimate the glass transition temperature. Then, both MD-predicted and experimental T_g value are inserted into the ECNLE theory to understand the intricate relationship between T_g and molecular dynamics. Our computational results are contrasted with experimental data in prior works to validate calculations and the approach. These findings are crucial for optimizing PEO's performance in its various applications.

2. Theoretical background of the ECNLE theory

As a brief introduction, we summarize the key aspects of the ECNLE theory. In this framework, a hard-sphere fluid is used to represent glass-forming liquids, characterized by the particle density, ρ, and particle diameter, d. The static structure factor, $S(q)$, and the radial distribution function, $g(r)$, are computed using the Percus-Yevick theory. The motion of a tagged particle is primarily influenced by interactions with its nearest neighbors, random noise, and a frictional force. These forces are governed by a nonlinear stochastic equation. Solving this equation yields the dynamic free energy, which quantifies the nearest-neighbor interactions

$$\frac{F_{dyn}(r)}{k_B T} = -3 ln\frac{r}{d} - \int_0^{\infty} dq \frac{q^2 d^3 [S(q)-1]^2}{12\pi\Phi[1+S(q)]} exp\left[-\frac{q^2 r^2 (S(q)+1)}{6S(q)}\right], (1)$$

where k_B is the Boltzmann constant, T is the ambient temperature, r denotes displacement, q is the wavevector, and $\Phi = \rho\pi d^3/6$ is the volume fraction. The first term corresponds to the caging constraint, while the second term is responsible for the ideal fluid state.

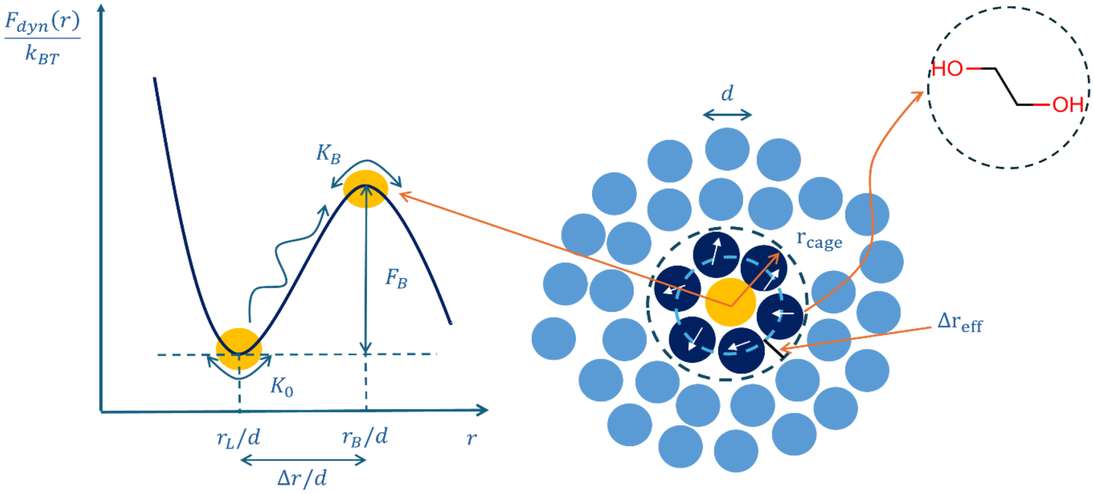

Figure 1. Schematic illustration of the dynamic free energy in the ECNLE theory. Key length and energy quantities are defined.

This free-energy profile provides essential physical quantities to describe local dynamics. In a dense system, the interparticle separation is reduced to form a particle cage, which dynamically restricts the movement of a central particle. The cage radius, r_{cage}, is determined as the position of the first minimum of $g(r)$. The onset of transient localization occurs when a local energy barrier appears in $F_{dyn}(r)$ as shown in Figure 1. The dynamic free energy has a local minimum and maximum at positions r_L and r_B, respectively. These values are used to calculate the barrier height, $F_B = F_{dyn}(r_B) - F_{dyn}(r_L)$, and the jump distance, $\frac{\Delta r}{d} = \frac{r_B}{d} - \frac{r_L}{d}$.

For a particle to escape its cage, both its nearest neighbors and the surrounding particles must reorganize to create additional space. As a result, collective motion is intrinsically linked to the local dynamics within the cage. This cooperative rearrangement induces a displacement field, $u(r)$, originating from the surface of the particle cage. This field triggers oscillatory motion in particles beyond the first coordination shell and propagates radially through the surrounding medium. Using Lifshitz's linear continuum mechanics, the displacement field for $r \geq r_{cage}$ can be analytically determined as: $u(r) = \frac{\Delta r_{eff} r_{cage}^2}{r^2}$ where Δr_{eff} is the amplitude of the field, whose explicit mathematical form has been previously reported (Mirigian et al., 2014a. 2014b, 2013). Given that $u(r)$ is relatively small, the oscillations of individual particles can be approximated as harmonic. This approximation allows us to assume the elastic energy of a single oscillator to be expressed as $K_0 u^2(r)/2$. To evaluate the impact of collective motion on the relaxation process, we sum the harmonic elastic energy contributions from particles outside the cage and this sum yields the collective elastic barrier

$$F_e = 2\pi\rho \int_{r_{cage}}^{\infty} dr\, r^2 g(r) K_0 u^2(r). (2)$$

By incorporating both local and elastic contributions into Kramers' theory, we obtain the structural relaxation time (Mirigian et al., 2013, 2014a. 2014b; Ngan et al., 2021; Phan et al., 2021, 2018b; Phan, Jedrzejowska, et al., 2020; Phan, Knapik-Kowalczuk, et al., 2019; Phan, Koperwas, et al., 2020; Phan, Wakabayashi, et al., 2019; Phan & Wakabayashi, 2020)

$$\frac{\tau_\alpha}{\tau_s} = 1 + \frac{2\pi}{\sqrt{K_0 k_B}} \frac{d^2}{k_B T} exp\left(\frac{F_B + F_e}{k_B T}\right), (3)$$

where τ_s is a short relaxation timescale. Its analytical expression has been reported in previous studies. The above formulation describes $\tau_\alpha(\Phi)$ but direct comparisons with experiments require converting density into temperature. Following earlier works (Mirigian et al., 2013, 2014 ; Ngan et al., 2021; Phan et al., 2021, 2018b; Phan, Jedrzejowska, et al., 2020; Phan, Knapik-Kowalczuk, et al., 2019; Phan, Koperwas, et al., 2020; Phan, Wakabayashi, et al., 2019; Phan & Wakabayashi, 2020), a thermal mapping based on the expansion process has been proposed

$$T = T_g + \frac{(\Phi_g - \Phi)}{\beta\Phi_0}, (4)$$

where T_g is the dynamic glass transition temperature, defined by $\tau_\alpha(T_g) = 100s$, and Φ_g is the corresponding volume fraction at which $\tau_\alpha(\Phi_g \approx 0.6157) = 100s$. Additionally, $\Phi_0 \approx 0.50$ is a characteristic volume fraction, and $\beta \approx 12 \times 10^{-4} K^{-1}$ represents an effective thermal expansion coefficient which is assumed to be constant across amorphous materials (Mirigian et al., 2013, 2014a. 2014b; Ngan et al., 2021; Phan et al., 2021, 2018b; Phan, Jedrzejowska, et al., 2020; Phan, Knapik-Kowalczuk, et al., 2019; Phan, Koperwas, et al., 2020; Phan, Wakabayashi, et al., 2019; Phan & Wakabayashi, 2020).

3. Molecular Dynamics Simulation

We perform atomistic molecular dynamics simulations to determine the glass transition temperature T_g of PEO using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS). The initial configuration consists of 40 PEO chains, each with a polymerization degree of N = 10. Periodic boundary conditions (PBCs) are applied in all three spatial directions to mimic bulk behavior. The repeating unit of a PEO chain is $-[CH_2 - CH_2 - O]_N -$. The molecular weight of each polymer chain is 458.55 g/mol, and the total number of atoms in the simulation system is 2920. The system is first thermalized at 320 K under isothermal-isobaric NPT conditions at 1 atm pressure. This temperature is selected to be below the melting point of PEO from 338 K (Money et al., 2013) to ensure that the polymer remains in the amorphous state. After thermalization, the system undergoes a stepwise cooling process from 320 K to 100 K to analyze the volume change with decreasing temperature. The cooling is performed in 10 temperature increments of 22 K each. At each temperature step, the system is equilibrated for 200000 steps with a time step of 0.5 fs, resulting in a total simulation time of 2200000 steps.

4. Results and discussion

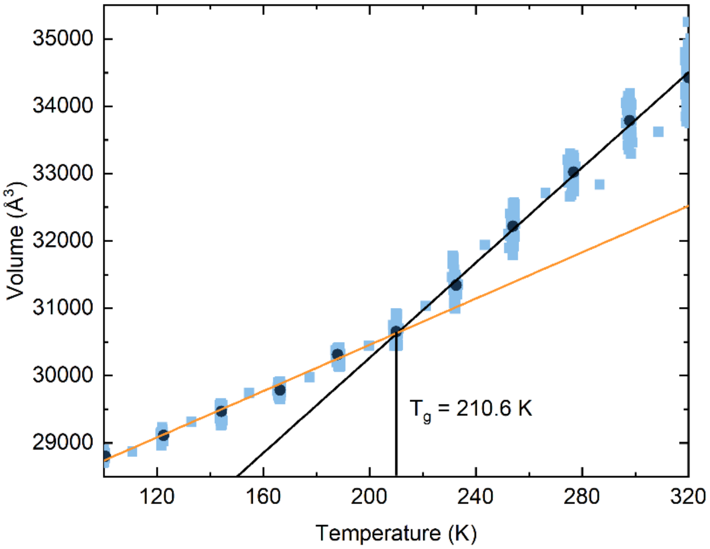

Figure 2. Volume as a function of temperature from MD simulations of PEO. The blue squares represent the raw simulation data at different temperatures, while the black markers denote the averaged volume values at corresponding temperatures. The black and yellow lines are linear fits at high and low-temperature regimes, respectively. The intersection of these two fitted lines determines the glass transition temperature (White et al., 2016).

Figure 2 shows our MD simulation results for the volume of the simulated cell as a function of temperature. By linearly fitting the averaged data in the low- and high-temperature regimes, we can see that the two lines cross each other at 210.6 K, and this is the glass transition temperature T_g. In our MD simulations, although the shorter chains may not fully capture long-range entanglement effects present in high-molecular-weight polymers, our study focuses on estimating the glass transition temperature T_g, primarily governed by segmental dynamics and local packing behavior rather than large-scale chain entanglement. Critically, our simulations yielded a T_g value of 210.6 K for PEO, which is in quantitative agreement with experimental values reported in the literature (Lunkenheimer et al., 2025; Vrandečić et al., 2010; Schmidt et al., 1998; Faucher et al., 1966), typically ranging from 211 K to 226 K. The difference in slope between the glassy and supercooled liquid regions provides insights into the material's thermodynamic properties. A steeper slope in the supercooled liquid region suggests enhanced atomic mobility, whereas the nearly constant slope in the glassy state reflects restricted molecular rearrangement.

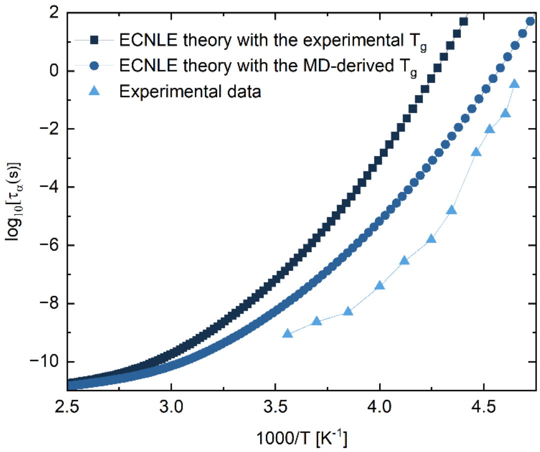

Figure 3. Logarithm of the experimental and theoretical structural relaxation time PEO as a function of 1000/T. Data triangles are experimental data in Ref (Lunkenheimer et al., 2025), circles correspond to our ECNLE predictions for the temperature-dependent relaxation times using the T_g values obtained from Fig. 2. and squares correspond to our ECNLE predictions for the temperature-dependent relaxation times using the T_g experimental values in Ref (Faucher et al., 1966).

After obtaining T_g from MD simulations, we plug in this value to Eq. (4) to convert from the volume fraction to temperature and apply the ECNLE calculations (Eq. (3)) to determine the temperature-dependent structural relaxation time of PEO. To validate our theoretical framework, we compare numerical results with experimental data extracted from Ref. *(Lunkenheimer et al., 2025)* as shown in Figure 3. Overall, our ECNLE calculations associated with the MD-derived T_g are quantitatively consistent with experiments and can be used to describe the thermal variation of the structural relaxation time of PEO.

In previous works (Mirigian et al., 2013, 2014a, 2014b ; Ngan et al., 2021; Phan et al., 2021, 2018b; Phan, Jedrzejowska, et al., 2020; Phan, Knapik-Kowalczuk, et al., 2019; Phan, Koperwas, et al., 2020; Phan, Wakabayashi, et al., 2019; Phan & Wakabayashi, 2020) , we have used the experimental T_g to construct the thermal mapping for the density-to-temperature conversion (Eq. (4)). Extrapolating experimental data in Ref. (Lunkenheimer et al., 2025) gives us $T_g = 211\,K$. If we use this value in our ECNLE calculations, numerical results perfectly overlap the results originating from a combination between the ECNLE theory and the MD-derived T_g shown in Figure 3. However, if we use the experimental T_g value from different techniques such as DMA reported by Faucher et al. (1966), the T_g is found to be 226 K. As illustrated in Figure 3, the theoretical curve is still close to experimental data, particularly in the high-temperature regime. Therefore, although longer chains could offer a more detailed picture of global polymer dynamics, the current chain length is adequate for capturing the essential physics governing T_g and for integrating with ECNLE theory. However, the large deviation can be seen in the low-temperature regime. We conducted a statistical analysis of the agreement between ECNLE-predicted relaxation times and experimental broadband dielectric spectroscopy data. Specifically, we computed the mean absolute error (MAE), root mean square error ($RMSE$), and coefficient of determination (R^2) between the τ_α

from ECNLE calculations (using both experimental- and MD-derived T_g values), and the corresponding experimental data across the studied temperature range. For ECNLE calculations using $T_{g,expt}$, MAE = 4.7223, RMSE = 4.8672, and R² = –1.7242. Meanwhile, for ECNLE calculations using $T_{g,MD}$, MAE = 1.8959, RMSE = 1.9587, and R² = 0.5588. These findings clearly indicate that our predictions with $T_{g,MD}$ are in excellent quantitative agreement with experiments. The strong correlation between theory and experiment underscores the robustness of ECNLE theory in describing the fundamental relaxation behavior of PEO.

PEO is a widely used host polymer in solid polymer electrolytes due to its ability to solvate lithium salts and form ion-conducting amorphous phases. However, ionic conductivity is tightly coupled to the segmental motion of the polymer chains governed by $\tau_\alpha(T)$. From these calculations, we can determine the structural relaxation time at room temperature (~298 K) and this allows us to quantitatively estimate ion mobility and design the formulation of PEO-based blends or composites to achieve desired performance metrics.

Similarly, for flexible and wearable electronic applications, the mechanical flexibility and dynamic response of PEO-based materials under thermal and mechanical stress are governed by their relaxation spectrum. Accurate prediction of $\tau_\alpha(T)$ across a broad range of temperatures helps predict time-dependent deformation, viscoelastic damping, and long-term stability of devices such as sensors and actuators fabricated from or encapsulated in PEO-based matrices.

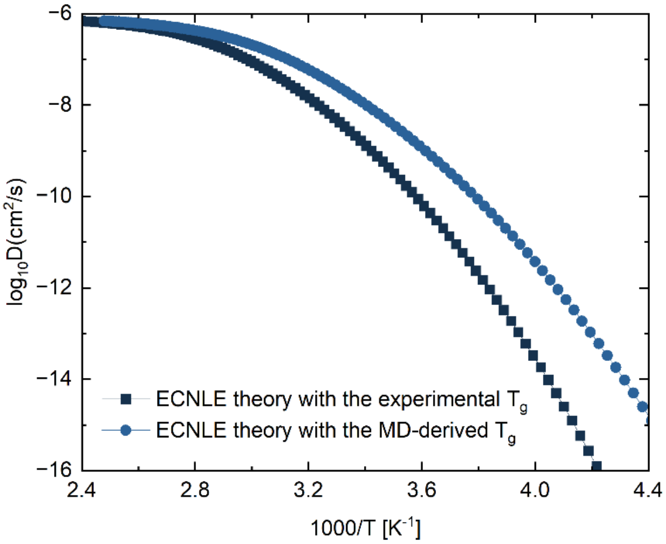

Figure 4. Logarithm of the experimental and theoretical diffusion coefficient PEO as a function of 1000/T. Circles correspond to our ECNLE predictions for the temperature dependence of the diffusion constant using the T_g values obtained from Fig. 2 and squares correspond to our ECNLE predictions for the temperature-dependent diffusion coefficient using the T_g experimental values in Ref. (Faucher et al., 1966).

According to ECNLE theory, the diffusion coefficient $D(T)$ and $\tau_\alpha(T)$ is related by

$$D(T) = \frac{\Delta r^2}{6\tau_\alpha(T)}, (5)$$

where Δr is the jump distance as shown in Figure 1. For PEO, our MD simulations estimate $d \approx 3.65$ Å. By substituting this value and the calculated $\tau_\alpha(T)$ from Figure 3 into the equation above, we obtain $D(T)$ as shown in Figure 4. These are new results and need experimental measurements to validate. However, in previous works (Ngan et al., 2021; Phan et al., 2022; Phan, Koperwas, et al., 2020), the temperature dependence of the diffusion constant determined using the ECNLE calculations is in quantitative accordance with experimental and simulation data. Thus, our calculations for the diffusion constant are reliable.

5. Conclusion and policy implications

In this paper, we have conducted a comprehensive investigation of the glass transition and structural relaxation dynamics in poly(ethylene oxide) using molecular dynamics simulations and the ECNLE theory. By accurately determining the glass transition temperature from MD simulations and applying the ECNLE framework, we successfully predicted the temperature-dependent behavior of structural relaxation time and diffusion constants. Our numerical results exhibit strong quantitative agreement with experimental data from previous studies and validate the effectiveness of our approach in capturing relaxation dynamics in polymers. This approach integrating atomistic simulations with statistical mechanical modeling provides deeper insights into polymer relaxation and diffusion across different timescales. Our findings contribute to a more fundamental understanding of the glass transition in polymeric materials and offer a robust framework for future studies on polymer dynamics.

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