Current Applied Science and Technology e-ISSN: 2586-9396

Curr. Appl. Sci. Technol. ….., Vol... (No...), e0263979

Research article

Thermodynamic and Structural Analysis of Proximity-Induced Transitions in Surface-Grafted Polymer Pairs

Porpieng Kullohamongkol[1], Papawarin Rattanaphun[1], Pakateema Sukhampeeranont[1], Santhad Pitakwongsaporn[2] and Busara Pattanasiri[2]*

[1]Kasetsart University Laboratory School, Kampaeng Saen Campus, Educational Research and Development Center, Nakhon Pathom, Thailand
[2]Division of Physics, Department of Physical and Material Sciences, Faculty of Liberal Arts and Science, Kasetsart University Kamphaeng Saen Campus, Nakhon Pathom, Thailand

Received: 10 July 2024, Revised: 14 April 2025, Accepted: 21 May 2025, Published: 1 September 2025

Abstract

This study aims to investigate structural transitions in grafted polymers by varying interpolymeric distance and surface interaction strength using coarse-grained modeling and parallel tempering simulations. We examine the behavior of two grafted polymers on a smooth surface, utilizing the flexible homopolymer model and parallel tempering simulations. Focusing on the interplay between distance separating the polymer chains and the strength of their interaction with the surface, we analyze thermodynamic quantities and structural parameters. Our results demonstrate that at larger interpolymeric distances, adsorption transitions from desorbed to adsorbed expand states are observed, followed by collapse and freezing transitions at lower temperatures. Increasing surface interaction strength shifts these transitions to higher temperatures. At smaller interpolymeric distances, the polymers remain entangled, preventing the observation of collapse transitions and resulting in only adsorption transitions at higher temperatures and freezing transitions at lower temperatures. Without surface attraction, only collapse and freezing transitions are observed. These findings emphasize the importance of structural thermodynamic quantities in identifying these transitions and highlight the significant role of interpolymeric distance and surface interaction strength in the behavior of grafted polymers. This study provides valuable insights for designing and optimizing polymer-grafted surfaces, contributing to advancements in materials science and engineering.

Keywords: structural transitions; Monte Carlo simulation; parallel tempering simulations; grafted polymers; flexible homopolymer model

---

*Corresponding author: E-mail: faasbrp@ku.ac.th
https://doi.org/10.55003/cast.2025.263979

1. Introduction

The study of polymer chains grafted onto solid surfaces has garnered significant attention across various research fields. Applications include enhancing the biocompatibility of biomaterials, stabilizing colloidal dispersions, and improving adhesion in polymers (Midya et al., 2020). Integrating polymers with layered inorganic materials like graphene and carbon nanotubes has been explored to enhance electrical and mechanical properties, thermal stability, and chemical resistance (Holt et al., 2016). Understanding the behavior of adsorbed polymers under diverse environmental and surface conditions is crucial for developing advanced materials and innovative technological applications (Zhang et al., 2024).

Our previous work investigated the influence of pattern recognition effects on the adsorption behavior of a flexible elastic polymer using generalized-ensemble Monte Carlo simulations (Pattanasiri et al., 2015). By comparing the adsorption of polymers on a uniform, unstructured substrate with that on a hexagonal surface pattern mimicking a graphene sheet, we identified significant structural phases and constructed hyperphase diagrams of adsorption. This study highlighted the complexity of interactions among atoms or monomers, which typically results in a rough free-energy landscape, making simulations challenging.

Building upon our prior research, this work aims to provide a comprehensive analysis of the structural transitions of two flexible homopolymer chains grafted onto a homogeneous surface. We employ a coarse-grained model that simplifies polymer chains by representing groups of atoms or monomers as single beads (Liewehr & Bachmann, 2019). This approach allows for efficient simulations while retaining essential features of polymer flexibility and interactions. Parallel tempering simulations are utilized to enhance sampling efficiency, particularly for systems with complex energy landscapes where traditional Monte Carlo simulations may struggle to overcome energy barriers (Marinari & Parisi, 1992).

Our focus is on the interplay between the distance separating the polymer chains and the strength of their interaction with the surface. By analyzing thermodynamic quantities and structural parameters, we aim to identify and characterize the transitions between different structural states. The findings from this study provide key insights into the dynamic behavior of grafted polymers, highlighting the importance of structural thermodynamic quantities in identifying these transitions.

Therefore, the main objective of this study is to investigate how varying the interpolymeric distance and surface interaction strength influence the thermodynamic and structural transitions of two flexible homopolymers grafted onto a homogeneous surface. We hypothesize that increasing the surface interaction strength will shift the adsorption, collapse, and freezing transitions to higher temperatures, and that smaller interpolymeric distances will lead to significant entanglement effects, preventing typical collapse transitions. These findings will not only advance our understanding of polymer-surface interactions but also provide guidelines for designing polymer-grafted surfaces with tunable properties in materials science and engineering (Mavrantzas, 2021; Bhayo et al., 2022; Qi et al., 2022; Conrad & Robertson, 2023; Gao et al., 2024; Wu et al., 2024).

2. Materials and Methods

2.1 Coarse-grained model for flexible polymers

In this study, we employ the coarse-grained model for two flexible polymers grafted onto a homogeneous surface. This approach simplifies the complexity of the polymer chains by representing groups of atoms or monomers as single beads. This reduction allows for efficient simulations of larger systems over longer timescales while retaining the essential features of polymer flexibility and interactions. Compared to atomistic models, the coarse-grained approach significantly enhances computational efficiency, enabling simulation of larger systems and extended timescales. However, it may oversimplify specific atomic-level details, such as precise local dynamics or interactions, limiting direct comparability with experimental data at molecular resolution. The total energy of the system in a conformation X is expressed as the sum of bond energy (U_{B}), non-bonded interaction energy (U_{NB}), and surface interaction energy (U_{S}):

$$E(X) = U_{\mathrm{B}} + U_{\mathrm{NB}} + U_{\mathrm{S}} \tag{1}$$

The bond energy represents the interactions between adjacent beads in the polymer chain. This energy is described by the finitely extensible nonlinear elastic (FENE) potential combined with the Lennard-Jones potential (LJ), with the minimum located at r_0. This combination ensures that the beads remain connected while allowing for flexibility and preventing overstretching. The bonded interactions are thus given by:

$$U_{\mathrm{B}} = U_{\mathrm{FENE}} + U_{\mathrm{LJ}} - U_{\mathrm{shift}}\ . \tag{2}$$

The finitely extensible nonlinear elastic potential U_{FENE} with the minimum located at r_0 is

$$U_{\mathrm{FENE}} = -\frac{1}{2}KR^2\ln\left[1-\left(\frac{r-r_0}{R}\right)^2\right], \tag{3}$$

where R = 3/7 r_0 is the maximum extension for the FENE potential, and K = 98/5 is the spring constant for the FENE potential. The Lennard-Jones potential U_{LJ} is described by:

$$U_{\mathrm{LJ}} = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right], \tag{4}$$

where r is the distance between adjacent beads, $\sigma = 2^{-1/6}\, r_0$ is the Van der Waals distance associated with the potential minimum at r_0, and ε is the depth of the Lennard-Jones potential well. U_{shift} is the shifted Lennard-Jones potential at $r = r_c$ to avoids a discontinuity at r_c. In our simulations, we set both r_0 and $\varepsilon = 1$.

The non-bonded interaction energy captures the Van der Waals forces between non-adjacent beads within the same polymer and between different polymers. This energy is modeled using the Lennard-Jones potential, which includes both attractive and repulsive components:

$$U_{\mathrm{NB}} = \begin{cases} U_{\mathrm{LJ}} - U_{\mathrm{shift}}\,, & r < r_c, \\ 0, & \text{otherwise.} \end{cases} \tag{5}$$

The surface interaction energy represents the interactions between the polymer beads of two polymers and the grafting surface. Since, the first monomer is grafted onto the surface, it is only calculated for monomers 2 to N. This term is crucial for modeling adsorption and desorption behaviors, as it reflects the attractive and repulsive forces between the beads and the surface:

$$U_\mathrm{S} = \varepsilon_S \sum_{i=2}^{N} \left[\frac{2}{15}\left(\frac{1}{z_i}\right)^9 - \left(\frac{1}{z_i}\right)^3\right] \tag{6}$$

where ε_S is the surface interaction strength and z_i is the distance of bead i from the surface. Here, we simulated two grafted homopolymer, each with $N = 20$ monomers, with surface interaction strength $\varepsilon_\mathrm{S} = [0,3]$, and the distance between adjacent polymer chains $d = [5,10]$.

2.2 Parallel tempering

Parallel tempering, also known as replica exchange Monte Carlo, is a powerful simulation technique employed to enhance the sampling efficiency of systems with complex energy landscapes. This method is particularly effective for studying systems where traditional Monte Carlo simulations may struggle to overcome energy barriers, leading to incomplete sampling of the phase space. Parallel tempering efficiently overcomes energy barriers by allowing configuration exchanges between replicas at different temperatures, thus facilitating sampling of states that would be kinetically inaccessible in traditional single-temperature simulations. This ensures comprehensive exploration of the energy landscape, crucial for accurately identifying structural transitions in polymer systems.

The simulation begins with the initialization of multiple replicas of the system, each at a distinct temperature. For this study, 35 replicas were used, with temperatures uniformly distributed between 0.1 and 3.0. This range ensures comprehensive sampling across both low-energy and high-energy states, providing a robust exploration of the system's phase space. Each replica evolves independently according to its assigned temperature. Unlike conventional Metropolis sampling, which simulates the system at a fixed temperature, parallel tempering leverages a generalized-ensemble approach. The acceptance probability for a new configuration in each replica is determined by the Metropolis criterion:

$$P_\mathrm{accept} = \min\left(1, \exp\left(-\frac{E_\mathrm{new} - E_\mathrm{old}}{k_B T_i}\right)\right), \tag{7}$$

where T_i is the temperature of the i-th replica, and E_new and E_old are the energies of the new and old configurations, respectively. Here, we set Boltzmann constant $k_\mathrm{B} = 1$. At every $n = 10^3$ intervals, and we attempt to exchange configurations between pairs of adjacent replicas with

$$P_\mathrm{exchange} = \min\left(1, \exp\left(\frac{1}{T_i} - \frac{1}{T_j}\right)\left(E_i - E_j\right)\right), \tag{8}$$

where T_i and T_j are the temperatures and E_i and E_j are the energies of replicas i and j, respectively. A schematic representation of parallel tempering is shown in Figure 1.

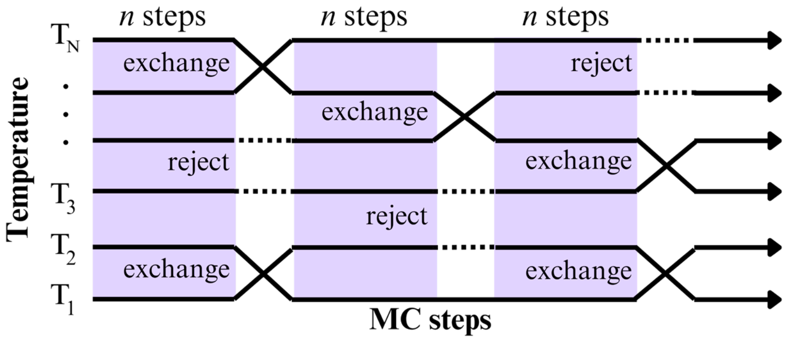

Figure 1. Schematic representation of parallel tempering swaps between adjacent replicas at different temperatures

The simulation process, including independent evolution and exchange attempts, is repeated for a sufficient number of iterations to ensure comprehensive sampling. In this study, the simulations are run for up to 10^7 Monte Carlo steps. This extensive iteration allows for a detailed exploration of the system's energy landscape, capturing both equilibrium and non-equilibrium states.

2.3 Statistical analysis

We analyze a multitude of energetic and structural thermodynamic quantities and their fluctuations to identify pronounced features indicating structural transitions in the grafted polymers system. The most general quantity is the specific heat, C_V, where its peaks often correspond to significant changes in the system's structural or thermodynamic state. The specific heat can be obtained from:

$$C_{\mathrm{V}}(T) = \frac{1}{k_B T^2}(\langle E^2 \rangle - \langle E \rangle^2). \tag{9}$$

The radius of gyration of each polymer in the direction parallel ($R_{g\parallel}$) and perpendicular ($R_{g\perp}$) to the surfaces provide insights into the polymer's size and shape that changes under different conditions. They are defined as:

$$R_{g\parallel} = \sqrt{\frac{1}{N}\sum_{i=1}^{N}[(x_i - x_{cm})^2 + (y_i - y_{cm})^2]}, \tag{10}$$

and

$$R_{g\perp} = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(z_i - z_{cm})^2}, \tag{11}$$

where x_{cm}, y_{cm}, and z_{cm} are the center of mass of the polymer in x, y, and z directions, respectively.

The number of surface contacts, n_S, is a useful tool for indicating the degree of adsorption transitions. In this case, we count the number of polymer beads in contact with the surface when the spatial component $z_i \leq 1.5$.

3. Results and Discussion

We find ten major structural configurations, namely: desorbed expand (DE), adsorbed expand (AE), desorbed globule (DG), adsorbed globule (AG), adsorbed compact (AC), entangled desorbed expand (EDE), entangled adsorbed expand (EAE), entangled desorbed globule (EDG), entangled adsorbed globule (EAG), and entangled adsorbed compact (EAC). Representative examples of the conformations are shown in Figure 2. It should be noted that the adsorbed compact (AC) state can further be divided into one-layer or multiple-layer configurations. Specifically, the desorbed expand (DE) conformation represents polymers fully extended away from the surface with minimal or no contact. In the adsorbed expand (AE) conformation, polymers spread out broadly while adhering closely to the surface. The desorbed globule (DG) describes collapsed, spherical shapes detached from the surface, whereas the adsorbed globule (AG) is similar but adhered directly to the surface. The adsorbed compact (AC) conformation is a densely packed arrangement directly on the surface, which can be further differentiated into single-layer or multilayered structures. For smaller interpolymeric distances, polymer chains become significantly intertwined, forming entangled states: entangled desorbed expand (EDE) and entangled adsorbed expand (EAE) indicate extended yet entangled structures detached or adhered to the surface, respectively. Similarly, the entangled desorbed globule (EDG) and entangled adsorbed globule (EAG) represent entangled compact shapes away from or attached to the surface. Lastly, the entangled adsorbed compact (EAC) conformation denotes densely packed, strongly entangled polymer arrangements closely bound to the surface.

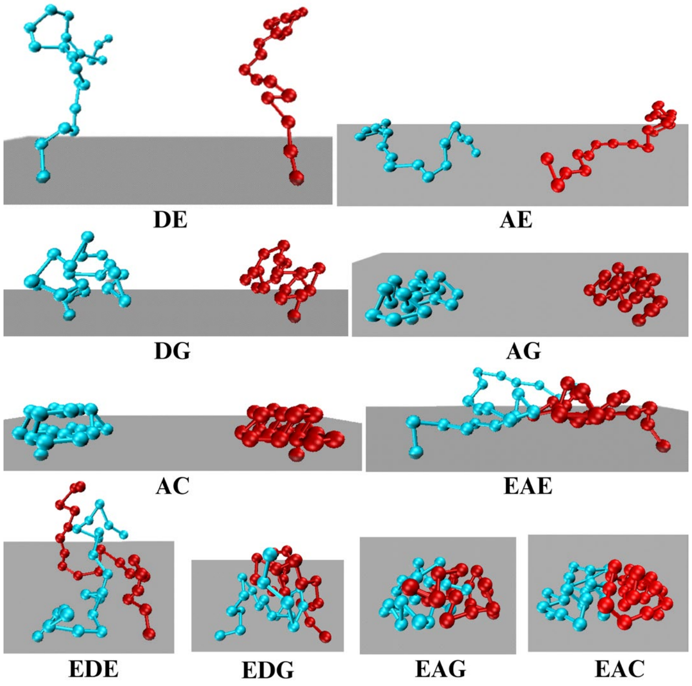

Figure 2. Representative examples of ten major conformations for two polymers, each with N = 20 monomers, grafted on a homogeneous surface.

Figure 3 shows the specific heat and the thermal derivatives of the radius of gyration for each polymer in both the parallel ($R_{g\parallel}$) and perpendicular ($R_{g\perp}$) directions relative to the surface, as well as the number of surface contacts (n_S), as functions of temperature (T). These measurements are presented for two polymers grafted onto a surface, with varying surface interaction strengths (ε_S), for interpolymeric distances of d = 5 and d = 10. Distinct peaks and shoulders observed in these measurements indicate conformal transitions between various structural macrostates of the system. For example, during an adsorption transition (DE→AE), the radius of gyration perpendicular to the surface ($R_{g\perp}$) markedly decreases, which is accompanied by a noticeable dip in the derivative of surface contacts (dn_S/dT). A collapse transition (AE→AG) is indicated by distinct peaks in the parallel radius of the gyration derivative ($dR_{g\parallel}/dT$), reflecting polymer compression in the surface plane.

Physically, the shift of adsorption/collapse/freezing transitions to higher temperatures can be understood by considering that increased surface attraction reduces the system's free energy more effectively, making polymer segments more likely to adsorb. Consequently, the temperature at which competing entropic effects overcome this attraction is shifted upward.

When the interpolymeric distance d = 10 and both the temperature (T) and surface interaction strength (ε_S) are nonzero, as shown in Figure 3 (e)-(h), an adsorption transition from desorbed expand (DE) to adsorbed expand (AE) occurs. This transition can be characterized by the peak in the thermal derivatives of the radius of gyration perpendicular to the surfaces ($dR_{g\perp}/dT$) and the dip in the number of surface contacts (dn_S/dT) at higher temperatures. As the temperature decreases, a collapse transition from adsorbed expand (AE) to adsorbed globule (AG) occurs, which can be observed from the peak in $dR_{g\parallel}/dT$ at approximately $T \approx 0.5-1.25$. Increasing ε_S results in a higher adsorption transition temperature and a lower collapse transition temperature. In this case, the adsorption transition is difficult to observe from specific heat (C_v). Therefore, using structural thermodynamic quantities to identify this transition is crucial. Around $T \approx 0.25$, a freezing transition from adsorbed globule (AG) to adsorbed compact (AC) is observed, which is signified by the peak in both specific heat (C_v) and $dR_{g\parallel}/dT$ or the dip in $dR_{g\perp}/dT$.

In the absence of attractive forces between the surface and the polymer, the only interactions present are those between the monomers themselves. Consequently, there is no adsorption transition. The structural change observed at $T \approx 1.1$ is a collapse transition, changing from desorbed expanded (DE) to desorbed globule (DG). Additionally, at $T \approx 0.25$, a freezing transition occurs from desorbed globule (AG) to adsorbed compact (AC). These observations are similar to findings in other studies (Möddel et al., 2011; Liewehr & Bachmann, 2016).

Similar behavior is observed for d = 5, as shown in Figure 3 (a)-(d). However, due to the smaller interpolymeric distance, the polymers remain entangled throughout. This entanglement prevents the observation of a collapse transition in the x-y direction, resulting in the absence of a peak in $dR_{g\parallel}/dT$. Therefore, at higher temperatures, only an adsorption transition from entangled desorbed expand (EDE) to either entangled adsorbed expand (EAE) or entangled desorbed globule (EDG), depending on the value of the surface attractive forces, is observed. This is followed by a freezing transition to entangled adsorbed compact (EAC) at around $T \approx 0.25$. As found for d = 10, increasing ε_S also shifts the adsorption transition to higher temperatures. When $\varepsilon_S = 0$, no adsorption occurs, but a collapse transition from entangled adsorbed expand (EAE) to entangled desorbed globule (EDG) is observed.

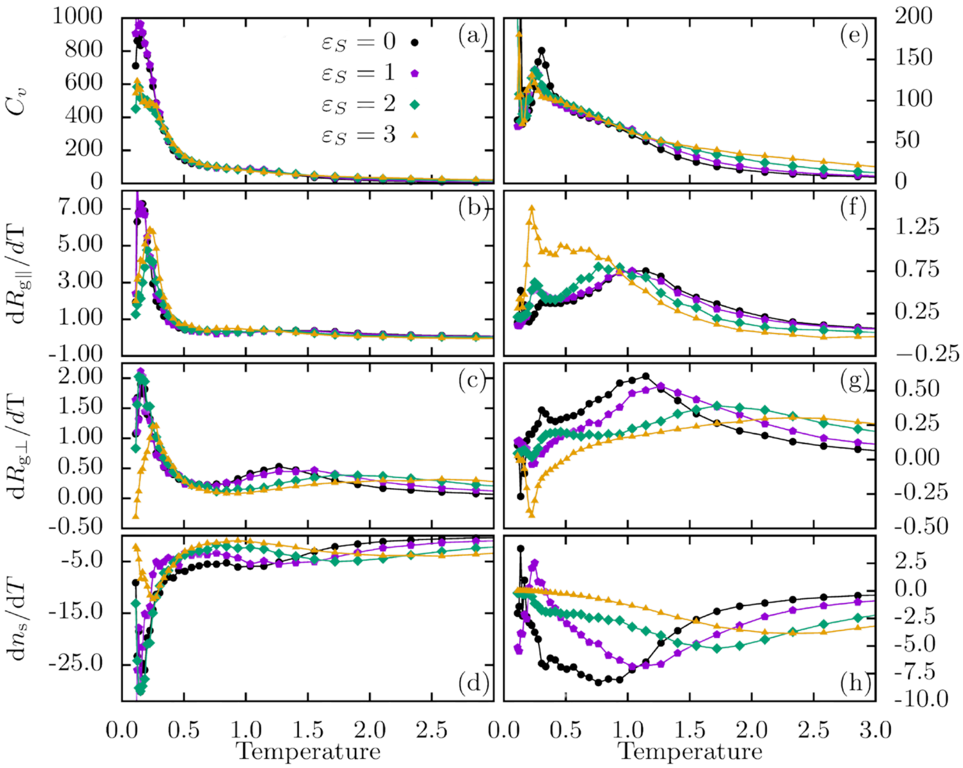

Figure 3. Analysis of two polymers grafted onto a surface with varying surface interaction strengths (ε_S), shown for (a)-(d) *d* = 5 and (e)-(h) *d* = 10, respectively. Error bars smaller than the data point are not shown.

The observed shift to higher transition temperatures with increased surface interaction strength (ε_S) occurs because stronger surface attractions energetically stabilize adsorbed states. At smaller interpolymeric distances, entanglement physically restricts polymer motion, preventing the collapse transitions due to limited spatial freedom, thus significantly altering the system's thermodynamic behavior.

4. Conclusions

In this work, we provide a comprehensive analysis of the structural transitions of two grafted polymers on a homogeneous surface using a flexible homopolymer model and parallel tempering simulations. We identified ten distinct structural configurations, with transitions highly dependent on interpolymeric distance, temperature, and surface interaction strength.

At larger distances, adsorption transitions were observed from desorbed to adsorbed expand states, followed by collapse and freezing transitions at lower temperatures. Increasing surface interaction strength shifted these transitions to higher temperatures. These transition shifts also correlated with increasing surface interaction strength. However, without surface attraction, only collapse and freezing transitions occurred. For smaller distances, entanglement hindered collapse transitions, leaving only adsorption transitions at higher temperatures and freezing transitions at lower temperatures.

Overall, the study enhances our understanding of the dynamic structural transitions of surface-grafted polymers, highlighting the importance of structural thermodynamic quantities in identifying these transitions.

5. Acknowledgements

Porpieng Kullohamongkol, Papawarin Rattanaphun, and Pakateema Sukhampeeranont were sponsored by Science Classrooms in University-Affiliated School Project at Kasetsart University Kamphaeng Saen Campus. This work was partially supported by a research grant from Division of Physics, Faculty of Liberal Arts and Science, Kasetsart University Kamphaeng Saen Campus.

6. Authors’ Contributions

The original idea was conceived by Busara Pattanasiri. Porpieng Kullohamongkol, Papawarin Rattanaphun, and Pakateema Sukhampeeranont contributed to the planning of the simulations and carried out the computations. All authors participated in the analysis of the results, provided critical feedback, and contributed to the preparation and revision of the manuscript.

7. Conflicts of Interest

The authors declare no conflicts of interest.

ORCID

Busara Pattanasiri https://orcid.org/0000-0002-9339-5886

References

Bhayo, A. M., Yang, Y., & He, X. (2022). Polymer brushes: Synthesis, characterization, properties and applications. *Progress in Materials Science*, 130, Article 101000. https://doi.org/10.1016/j.pmatsci.2022.101000

Conrad, J. C., & Robertson, M. L. (2023). Shaping the structure and response of surface-grafted polymer brushes via the molecular weight distribution. *Jacs Au*, 3(2), 333-343. https://doi.org/10.1021/jacsau.2c00638

Gao, H., Yu, Z., Zhang, X., Yu, X., Xing, J., Zhu, Y., Qian, H.-J., & Lu, Z.-Y. (2024). A mini review of the recent progress in coarse-grained simulation of polymer systems. *Chinese Journal of Structural Chemistry*, 43(5), Article 100266. https://doi.org/10.1016/j.cjsc.2024.100266

Holt, A. P., Bocharova, V., Cheng, S., Kisliuk, A. M., White, B. T., Saito, T., Uhrig, D., Mahalik, J. P., Kumar, R., Imel, A. E., Etampawala, T., Martin, H., Sikes, N., Sumpter, B. G., Dadmun, M. D., & Sokolov, A. P. (2016). Controlling interfacial dynamics: Covalent bonding versus physical adsorption in polymer nanocomposites. *ACS Nano*, 10(7), 6843-6852. https://doi.org/10.1021/acsnano.6b02501

Liewehr, B., & Bachmann, M. (2016). Homopolymer adsorption on hexagonal surfaces: A replica-exchange Monte Carlo study. *Journal of Physics: Conference Series*, 686(1), Article 012002. https://doi.org/10.1088/1742-6596/686/1/012002

Liewehr, B., & Bachmann, M. (2019). Smart polymeric recognition of a hexagonal monolayer. *Europhysics Letters*, 127(6), Article 68003. https://doi.org/10.1209/0295-5075/127/68003

Marinari, E., & Parisi, G. (1992). Simulated tempering: a new Monte Carlo scheme. *Europhysics Letters*, 19(6), Article 451. https://doi.org/10.1209/0295-5075/19/6/002

Mavrantzas, V. G. (2021). Using Monte Carlo to simulate complex polymer systems: Recent progress and outlook. *Frontiers in Physics*, 9, Article 661367. https://doi.org/10.3389/fphy.2021.661367

Midya, J., Rubinstein, M., Kumar, S. K., & Nikoubashman, A. (2020). Structure of polymer-grafted nanoparticle melts. *ACS Nano*, 14(11), 15505-15516. https://doi.org/10.1021/acsnano.0c06134

Möddel, M., Janke, W., & Bachmann, M. (2011). Comparison of the adsorption transition for grafted and nongrafted polymers. *Macromolecules*, 44(22), 9013-9019. https://doi.org/10.1021/ma201307c

Pattanasiri, B., Liewehr, B., & Bachmann, M. (2015). Surface pattern effects upon polymer adsorption. *Physics Procedia*, 68, 105-109. https://doi.org/10.1016/j.phpro.2015.07.117

Qi, H.-K., Yang, X., Yang, Q.-H., & Luo, M.-B. (2022). Effect of grafting density on the adsorption of end-grafted polymer chains. *Polymer*, 259, Article 125330. https://doi.org/10.1016/j.polymer.2022.125330

Wu, Y., Wang, Q., Sun, H., Wang, S., Han, Z., Chen, J., Wu, Z., Li, H., He, J., & Jiang, N. (2024). Recent advancements in experimental methods for investigating irreversible chain adsorption at polymer-solid interfaces. *Polymer*, 304, Article 127144. https://doi.org/10.1016/j.polymer.2024.127144

Zhang, A. C., Ohno, K., & Composto, R. J. (2024). Film thickness dependence of surface and internal morphology evolution in polymer-grafted nanocomposites. *Macromolecules*, 57(14), 6634-6645. https://doi.org/10.1021/acs.macromol.4c00854