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Molecular Simulation-Guided and Physics-Informed Mechanistic Modeling of Multifunctional Polymers

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Abstract Polymeric materials have a broad range of mechanical and physical properties. They have been widely used in material science, biomedical engineering, chemical engineering, and mechanical engineering. The introduction of active elements into the soft matrix of polymers has enabled much more diversified functionalities of polymeric materials, such as self-healing, electroactive, magnetosensitive, pH-responsive, and many others. To further enable applications of these multifunctional polymers, a mechanistic modeling method is required and of great significance, as it can provide links between materials' micro/nano-structures and their macroscopic mechanical behaviors. Towards this goal, molecular simulation plays an important role in understanding the deformation and evolution of polymer networks under external loads and stimuli. These molecular insights provide physical guidance in the formulation of mechanistic-based continuum models for multifunctional polymers. In this perspective, we present a molecular simulation-guided and physics-informed modeling framework for polymeric materials. Firstly, the physical theory for polymer chains and their networks is briefly introduced. It serves as the foundation for mechanistic-models of polymers, linking their chemistry, physics, and mechanics together. Secondly, the deformation of the polymer network is used to derive the strain energy density functions. Thus, the corresponding continuum models can capture the intrinsic deformation mechanisms of polymer networks. We then highlight several representative examples across multiphysics coupling problems to describe in detail for this proposed framework. Last but not least, we discuss potential challenges and opportunities in the modeling of multifunctional polymers for future research directions.

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1 Introduction

Over recent years, there have been extensive research efforts and progress in soft matter, with a broad range of applications in flexible and stretchable electronics in wearable devices [130, 153, 208, 206], deformable lighting or display devices [83, 78], actuators for soft robotics [171, 68, 84], artificial skin [150, 167, 56], and hydrogels in biomedical devices [8, 145, 61, 184, 88], to name a few. These devices take advantage of polymeric materials, such as polydimethylsiloxane (PDMS), poly(vinyl alcohol) (PVA), and poly(glycerol sebacate) (PGS), as the polymer matrix can provide desired mechanical properties in operation and biocompatibility for biomedical applications. Under external loadings, these materials display many typical mechanical behaviors such as strain softening/hardening, state-dependent, nonlinearity, and Mullins effect, etc. [35]. Besides, for many other applications, these polymers are further designed to be stimulus-responsive with multifunctionality, triggered by different mechanisms, such as an electric field [49, 142], magnetic field [106, 129], chemicals (*e.g.* pH) [143, 33], and thermal input [125, 85], among others. The multi-physics induced mechanical behaviors are even more complicated with typical examples summarized in Fig. 1.

The increasing demand for these polymers calls for the fast and accurate evaluation of their mechanical properties under multi-physics coupling effects, even before they actually deployed or manufactured [16]. Mechanical modeling allows for cheaper and faster predictions than experimental approaches alone, and thus, facilitates rapid evaluation of material properties and materials design. Historically, phenomenological models have been widely used for simulations of rubber-like polymers at the continuum level [117], which has been very successful to certain degrees. For example, it has inspired the development of hyperelasticity theories for elastomers [116, 62, 14]. Nevertheless, the material parameters in these phenomenological models usually do not have direct physical meanings. They are mostly defined based on internal variables for the mathematical fitting of experimental stress-strain curves, and thereby losing connections to underlying material's chemistry and microstructure [62, 146]. As a result, phenomenological models can only enable the evaluation of material properties [90].

Mechanistic models, on the other hand, can facilitate inverse materials design, as they contain the intrinsic micro/nanostructures and physical mechanisms [97, 212, 98, 16]. Usually, the material parameters in these mechanistic models bear physics meanings, which are signatures of polymer chemistry, physics, or dynamics. Thus, they can be further utilized to guide the inverse design of high-performance materials with tailored properties. To develop a mechanistic-based and physics-informed model across various physics and scales, the intrinsic micro/nanostructural features of polymers should be considered, leading to a meaningful structure-property relationship[75, 16]. Thus, it is very crucial that the microscopic features of polymer chains and networks are studied and integrated into a continuum constitutive model through multiscale modeling methods.

At the molecular level, polymers are composed of long-chain molecules, covalently bonded by a large number of repeat units. They have diverse physical and mechanical properties, due to the almost infinite combinations of chemical elements, molecular structures, and synthesis conditions [48, 82, 23]. Thus, detailed understandings of polymer structure, composition, and dynamics are essential to accurately predict their deformation behaviors under complex loading conditions [17], such as combined mechanical and electrical loading.

To link the polymer chains/networks to a continuum model, a multiscale modeling strategy is needed. Multiscale modeling approaches include two types: concurrent scale-bridging approaches and hierarchical approaches [102]. The former approach tries to model the system with different yet coupled resolutions (atomistic and continuum scales) simultaneously; while the latter focuses on the modeling of a continuum scale with knowledge informed from the atomistic scale [97, 91, 98]. Since the concurrent scale-bridging approach is computationally demanding, in this work, we only focus on the hierarchical multiscale approach. That is, the deformation mechanisms of polymer chains and networks are studied through molecular simulations, and the information obtained is passed to the constitutive model at the continuum level.

Molecular simulations provide an effective way to study the polymer chains and networks on micro and nanoscales [91, 93, 94, 92], which cannot be easily approached by experimental techniques. It has flourished enormous breakthroughs in mechanics and material science fields. The success of these molecular simulations is twofold: on one hand, they can be used to validate the assumptions made in classical theories at the continuum level [98]; on the other hand, it brings new insights into the intrinsic deformation mechanism of polymeric materials and provides material parameters for continuum models [97]. Therefore, these molecular simulation-guided and physics-informed models are more robust and efficient in the evaluation of mechanical properties for different polymeric materials. Eventually, they can be used for the design of novel functional devices with tailored material properties.

This work aims to present a perspective on molecular simulation-guided and physics-informed mechanistic modeling of polymeric materials. We first introduce the physics of polymer chains and networks at the molecular level. Then, we compare the phenomenological models with mechanistic-based models, considering the physical behaviors of polymeric materials. By highlighting a few representative works, we discuss how to formulate mechanistic models for multifunctional polymers, based on their molecular deformation mechanisms. We envision that, with the help of molecular simulations, mechanistic models of polymeric materials across different scales and physics can be formulated. These models will enable a broad range of applications of multifunctional polymers, such as soft robotics, protective coatings, damping materials, drug-eluting stents, and many others.

2 Polymer Physics and Chemistry

Physics-informed mechanistic models tend to correlate the microscopic deformation behaviors of polymer chains and networks to their macroscopic mechanical behaviors [4, 14, 36]. Therefore, it is crucial that the properties of polymer chains and networks are fully examined, to develop a mechanistic-based model for polymeric materials. We should emphasize that since most of the aforementioned applications require the matrix to be rubber-like (highly deformable and stretchable), we only focus on the polymers with a low cross-linking degree, namely elastomers. In this section, the polymer composition, topology, statistics,

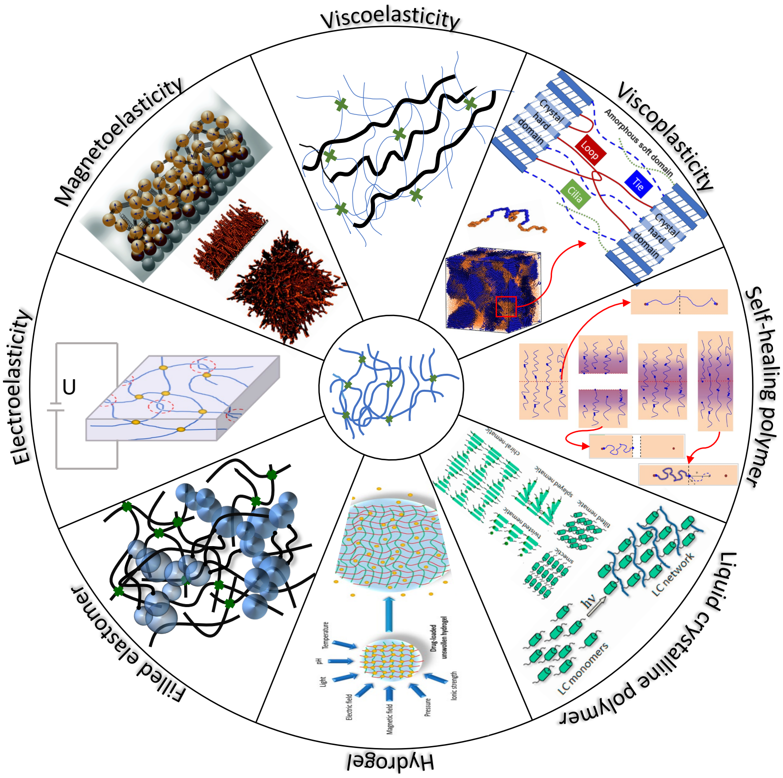

Fig. 1 Mechanistic modeling of polymeric materials, such as elastomers, semi-crystalline polymers, magnetorheological elastomers (the images are adapted from Ref. [138] with CCBY 3.0 license, copyright 2019 The Royal Society of Chemistry), electroactive polymers, filled elastomers, hydrogels (the image is adapted from Ref. [58] with CCBY 4.0 license, copyright 2018 MDPI publishing group), liquid crystal polymer (the image is reproduced from Ref. [100] with permission, copyright 2014 The American Chemical Society), and self-healing polymers (the images are adapted from Ref. [204] with permission, copyright 2018 Elsevier).

and dynamics will be briefly presented and is followed by the hyperelasticity formulation. With polymer hyperelasticity as the foundation, we can then incorporate more physical mechanisms and models to study the multifunctional polymers.

2.1 Polymer chains and networks

Different from metals and alloys, which are dominated by the internal energy change, the elasticity of polymers mainly originates from entropy change. This entropy change is a result of the conformation change of chains during deformation within the polymer network. When a polymer sample, *e.g.* elastomer, is stretched, the conformation change gives rise to the elastic deformation; after the loading is removed, the sample goes back to its initial state due to the effects of crosslinkers. Thus, the polymer network model plays a very important role in understanding polymer hyperelasticity.

The simplest model of a single polymer chain is the freely jointed chain (FJC), which ignores the interactions between monomers [132], as shown in Fig.2**a**. This long chain is formed by polymerization of n (polymerization degree) monomers with a bond length l. Since the chain's conformation is like a random walk, it is not needed to consider the absolute location of each monomer, rather than the statistics of the whole chain. An important quantity describing the chain is the end-to-end vector $\boldsymbol{R}_{ee} = \sum_1^N \boldsymbol{R}_i$. Since each bond is randomly oriented following the random walk, the statistical value (ensemble average over all possible conformations) of end-to-end vector is $\langle \boldsymbol{R}_{ee} \rangle = \boldsymbol{0}$. However, the mean squared end-to-end distance is nonzero but $\langle R_{ee}^2 \rangle = nl^2$, because there is no correlation between any two bond vectors. It must note that for linear chains using $\boldsymbol{R}_{ee}$ to quantify a polymer system is reasonable, but for nonlinear chains, *e.g.* ring chains, it is not suitable. Therefore, the radius of gyration $\langle R_g^2 \rangle = \frac{1}{N^2} \sum_{i=1}^N \sum_{j=1}^N \langle (\boldsymbol{R}_i - \boldsymbol{R}_j)^2 \rangle$ is more applicable.

FJC is an ideal polymer chain model. For real polymer chains, however, the motion of each bond may be constrained. In this case, other chain models have to be applied, such as the freely rotating chain (FRC) model, in which neighboring bonds have a constant angle. The characteristic ratio $C_n = \langle \boldsymbol{R}_{ee}^2 \rangle / nl^2$ is used to express the rigidity of the chain. This real chain can be converted to the equivalent FJC characterized by Kuhn length b and Kuhn steps N by maintaining the same mean squared end-to-end distance and maximum end-to-end distance $R_{\max}$ [132]. In what follows, the chains considered are the converted to Kuhn

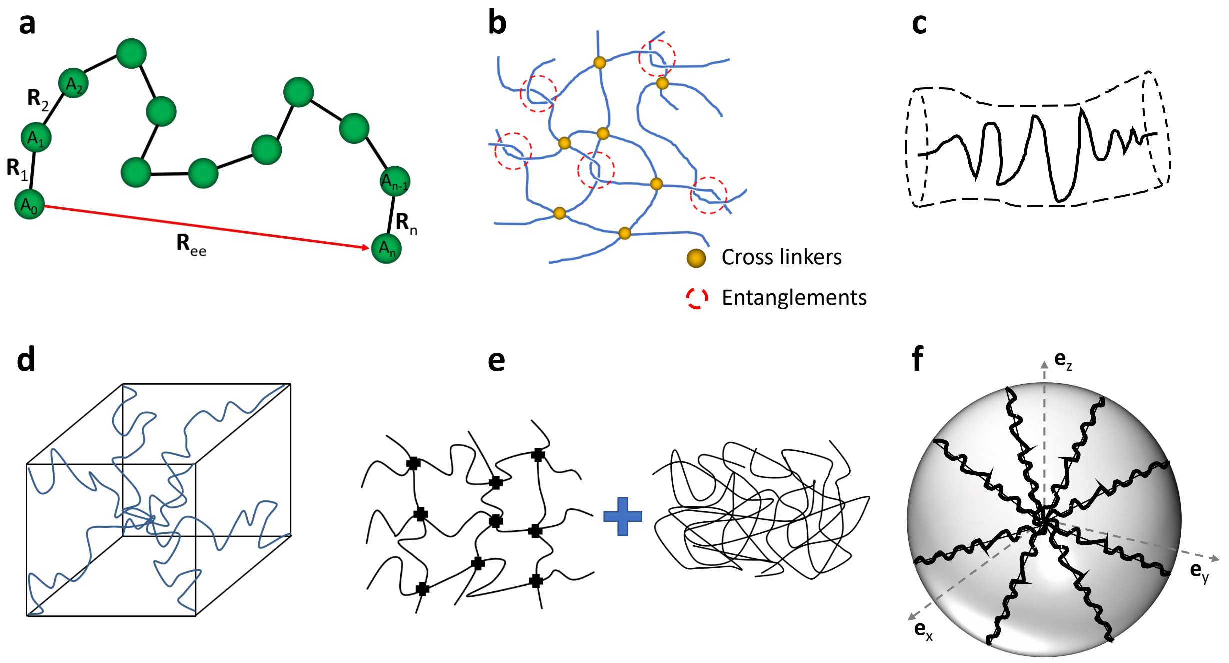

Fig. 2 Polymer networks and models. **a**: the conformation of a single freely jointed chain; **b**: polymer cross-links and entanglements in a polymer network; **c**: tube model for polymer entanglement analysis; **d**: eight-chain model for polymer network at undeformed configuration; **e**: Davidson-Goulbourne model for the decomposition of polymer network into cross-links and entanglements; **f**: Microsphere model for polymer network.

chains using Kuhn steps N and Kuhn length b from real chains (linear or nonlinear).

The Polymer network is composed of multiple chains. Fig.2**b** demonstrates a schematic of the polymer network. The individual chains are cross-linked together by cross-linkers (junction points) and can entangle together for long chains to form entanglements, which serve as physical cross-linkers. Due to the presence of neighboring chains, the motion of a single chain is restrained and characterized by a reptation motion constrained in a tube-like region [40], as illustrated in Fig. 2**c**. Cross-linkers and entanglements have significant roles in determining polymer elasticity, which will be presented in the next Section.

To quantify the conformation change of polymer network, the Gaussian chain statistics and Langevin chain statistics have been widely used, while the former is applied to describe the polymer network that is not extensively stretched (end-to-end distance $R_{ee} \ll Nb$) and the latter is for highly deformed polymer network. The Gaussian chain statistics [132] states that:

$$\Psi_G(N, R_{ee}) = C \exp(-\frac{3R_{ee}^2}{2Nb^2}) \tag{1}$$

where $\Psi_G(R_{ee})$ is the probability of the chain conformation with a end-to-end distance R_{ee} and C is a normalization constant. However, for polymer network experiencing large deformations, the Gaussian chain statistics does not hold anymore. In this case, the Langevin statistics establish:

$$\Psi_L(N, R_{ee}) = C \exp[-\frac{R_{ee}}{b}\beta(\frac{R_{ee}}{Nb}) - N \ln \frac{\beta(\frac{R_{ee}}{Nb})}{\sinh \beta(\frac{R_{ee}}{Nb})}] \tag{2}$$

where $\beta(x) = L^{-1}(x)$ is the inverse of Langevin function $L(x) = \coth(x) - 1/x$. This formulation enforces that the chains cannot be stretched excess the contour length Nb. Note that when R_{ee} is significantly less than the contour length Nb, the Langevin statistics in Eq. (2) reduces to the Gaussian statistics in Eq. (1).

2.2 Hyperelasticity of polymers

Rubber-like polymers are featured by significant reversibility and large stretchability. Phenomenological hyperelastic models have been widely employed to describe the deformation behavior of elastomers. For example, Ogden's model writes, for the strain energy density [116]:

$$W^{\text{Ogden}} = \sum_{p=1}^{N} \frac{\mu_p}{\alpha_p}(\lambda_1^p + \lambda_2^p + \lambda_3^p - 3) \tag{3}$$

where λ_i are macroscopic principal stretches with $\lambda_1\lambda_2\lambda_3 = 1$ to accommodate the incompressibility constraint, μ_p denotes the shear modulus, and α_p are material constants. Note that in these phenomenological models, the material parameters are not related to its intrinsic molecular or microstructures, and thus the model is phenomenological.

To construct a mechanistic-based model, it is important to link the polymer microstructures using *e.g.* polymer chain statistics to the Helmholtz free energy (F), which can be expressed by:

$$F(N, R_{ee}) = U(N, R_{ee}) - TS(N, R_{ee}) \tag{4}$$

where U is the internal energy, S the entropy of the system, and T the absolute temperature. The entropy of the system is calculated by:

$$S(N, R_{ee}) = k_B \ln \Omega(N, R_{ee}) \tag{5}$$

where k_B is the Boltzmann constant and Ω the number of possible chain conformations. The chain statistics Ψ relates to Ω through:

$$\Psi(N, R_{ee}) = \frac{\Omega(N, R_{ee})}{\int \Omega(N, R_{ee}) dR_{ee}} \tag{6}$$

One notices that the denominator in the above equation is a constant by the integration of R_{ee} and therefore is unrelated to R_{ee}. Thus, Eq. (5) can be rewritten as:

$$S(N, R_{ee}) = k_B \ln \Psi(N, R_{ee}) + S(N, 0) \tag{7}$$

Substituting Eq. (7) into Eq. (4), one derives:

$$F(N, R_{ee}) = -k_B T \ln \Psi(N, R_{ee}) + F(N, 0) \tag{8}$$

where $F(N, 0)$ is the free energy of the chain with zero end-to-end distance, which is the summation of the other terms in Eq. (4). In arriving at Eq. (8), the assumption of incompressibility constraint of polymers is applied, so that the internal energy change is neglected. Note that $F(N, 0)$ is only a constant irrelevant to the conformation and thus will be removed by taking a derivative to the deformation. Therefore, the free energy $F(N, R_{ee})$ is linked to the statistics $\Psi(N, R_{ee})$ of polymer chains.

Several micromechanics models, linking polymer chemistry and physics (kinematic variables in a single chain elasticity) to the macroscopic deformation measures, are summarized as follows. The most important postulation to develop these models is that the total free energy of the polymer network is the summation of free energy from all single strands [113, 34]. One will see that all the material parameters in these models have polymer physics or chemistry meanings. Note that though these micromechanics models enclose the molecular physics or chemistry of polymers, the assumptions made on the polymer system and deformation may not be realistic. Thus, they are only valid and generalizable to a certain extent and may not hold for other real polymer systems.

Affine network model. This model assumes that the junction points (cross-linkers) are fixed in an elastic non-fluctuating background [132]. Therefore, polymer chains deform affinely as to the macroscale deformation of the system, hence micro- stretch equals to macro-stretch homogeneously and isotropicly [187]. Additionally, it adopts the Gaussian chain statistics [14]. Considering a chain strand between two junction points and let N_c be the number of Kuhn steps between the two points, the deformed length and the underformed length are denoted as r and R. Then the following equations hold $r_i = \lambda R/\sqrt{3}$ $(i = 1, 2, 3)$ by decomposing the chain into three orthogonal directions, so that $\frac{3r_i^2}{2N_c b^2} = \frac{\lambda_i^2}{2}$, where λ is microstretch ratio. Thus, the strain energy density (free energy per unit volume) is contributed by all strands, which reads [36]:

$$W^{\text{affine}} = \frac{k_B T \rho_m}{2N_c}(\lambda_1^2+\lambda_2^2+\lambda_3^2-3) = \frac{G_c}{2}(\lambda_1^2+\lambda_2^2+\lambda_3^2-3) \tag{9}$$

where $G_c = k_B T \rho_m / N_c$ is the cross-link modulus, ρ_m is the monomer number density and λ_i $(i = 1, 2, 3)$ is the principal stretch of the polymer system in three principal directions. Since the affine network model is constructed upon Gaussian chain statistics, it does not work well for polymers undergoing large deformations [113].

Phantom network model. Different from the Affine network model, the phantom network model considers the fact that the junction points are subject to fluctuations, rather than fixed in the elastic non-fluctuating background [132]. Thus, the strand level deformation is not affine as the macro level. It assumes that there are two additional effective chains with length $n_p = N/(\phi - 2)$ (ϕ is the cross-linking functionality) participating in deformation along with the original chain [74, 133, 134]. The corresponding strain energy density is:

$$W^{\text{phantom}} = \frac{k_B T \rho_m}{2N_c}(1 - \frac{2}{\phi})(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) \tag{10}$$

$G_c = k_B T \rho_m (1 - \frac{2}{\phi})/N_c$ is the cross-linking modulus. One can see that, due to the fluctuations of the junction points, the modulus in this model is smaller (network is softer) than that in the Affine network model. Note that both the Affine network model and Phantom network model do not consider the topological entanglement constraint to polymer chains, and thus the modulus predicted in both models are less than that obtained from experiments.

Arruda-Boyce model. Arruda-Boyce model [4] is developed using Langevin chain statistics based on the eight-chain polymer network as shown in Fig. 2**d**. In this model, the affine deformation assumption holds. Namely, each chain in the network shares the same stretch as $\lambda_{\text{chain}} = \frac{1}{\sqrt{3}}(\lambda_1^2 + \lambda_2^2 + \lambda_3^2)^{1/2} = \frac{1}{\sqrt{3}}\sqrt{I_1}$, where I_1 is the first stretch invariant [4]. The strain energy density has the form of:

$$W^{\text{AB}} = \sum_i G_c \alpha_i (\frac{1}{\lambda_{\text{max}}^2})^{i-1}(I_1^i - 3^i) \tag{11}$$

where the first five coefficients are $\alpha_1 = 1/2$, $\alpha_2 = 1/20$, $\alpha_3 = 11/1050$, $\alpha_4 = 19/7000$, $\alpha_5 = 519/673750$ for numerical approximation of Langevin equation. The finite chain extensibility is $\lambda_{\text{max}} = \sqrt{N_c}$. Note that in this model, the chains are considered to move freely over each other. As a result, it cannot capture the topological constraint effect due to entanglements formed in long-chain polymers [113, 36, 98].

Davidson-Goulbourne model. This model considers both cross-linking effect by nonaffine phantom networks and the entanglement effect by the nonaffine tube model [36], which is simple in the formulation yet effective to capture large deformation behavior of elastomers. In this model, the strain energy density is formulated as:

$$W^{\text{DG}} = \frac{1}{6}G_c I_1 - G_c \lambda_{\text{max}}^2 \ln(3\lambda_{\text{max}}^2 - I_1) + G_e \sum_{i=1}^{3}(\lambda_i + \frac{1}{\lambda_i}) \tag{12}$$

where $G_e = \frac{4}{5}G_c N_c / N_e$ is the entanglement modulus [40, 98] and N_e is the entanglement length. Note that this model decouples the network into cross-links and entanglements and does not consider the interactions between them.

Micro-sphere model. This model [113] considers both affine and nonaffine deformations as well as entanglements effect but treats them differently from the Davidson-Goulbourne model. It assumes that the chains are oriented on the surface of a sphere, as shown in Fig. 2**f**. On the chain level, the model considers the stretch of each chain constrained by a microtube. The microscopic deformation (both affine and nonaffine) is accommodated by the homogenization procedure of the micro-variables on the microsphere. The total macroscopic response is the contributions from both the stretch and tube deformation. Note that in this model, there are five material parameters related to the network [113].

In summary, several representative mechanistic-based polymer network models are introduced. Note that there are requirements or limitations for these models to hold since they work under certain assumptions. For example, the transition between affine and phantom network models was observed in polymer gels [2]. Nevertheless, with the strain energy density function at hand, the stress can be easily derived by the relation between strain energy density and the strain measures. Consequently, constitutive modeling can be feasibly employed accordingly.

3 General Principles in Molecular Simulation-Guided and Physics-Informed Mechanistic Modeling

The micromechanics modeling approaches of polymer networks have been widely adopted. However, when the new physics is involved, *e.g.* external electric field, the development of a coupled electro-elastic strain energy density function is not trivial. In this case, the multiphysics coupling effects have to be incorporated. Then, the model can accurately capture the macroscopic deformation behaviors. Again, the key aspect is to examine the microscale deformation mechanism under multiphysics loading conditions, which can provide the intrinsic deformation mechanism and guide the formulation of continuum models. Thus, molecular simulations are particularly effective towards this goal.

3.1 Molecular simulations in mechanistic modeling of polymers

Molecular simulations offer an effective way to study down the atomic resolution of materials and link material chemistry to their mechanical properties [50]. They provide a beneficial strategy to deal with complex physical problems for which analytical solutions are not available. As a virtual laboratory platform, molecular simulations can be used to understand the contributions of each possible factor involved in a complicated system by well-controlled variables and designed systems. Therefore, we can leverage the physical mechanisms informed from molecular simulations to develop mechanistic-based models for polymeric materials.

In a molecular dynamics (MD) simulation, the system is composed of a set of particles carrying physical information, such as atoms in an all-atom system. The particles in the system follow Newton's second law of motion under the interaction forces from other particles, which includes bonded and non-bonded interactions. The force field derived from the potential energy defines the interaction between particles. The governing equation of motion can be formulated as:

$$m\ddot{\boldsymbol{r}} = \boldsymbol{F} = -\frac{\partial U(\boldsymbol{r})}{\partial \boldsymbol{r}} \tag{13}$$

where m and $\boldsymbol{r}$ are the mass and position of a particle, respectively. $U(\boldsymbol{r})$ is the energy function determining interactions between particles. $\boldsymbol{F}$ is the total force applied on the particle from other particles. In an MD simulation, this equation is solved by a numerical time integration so that the positions and velocities of all particles can be updated till a given time scale. Note that to capture specific motions of atoms or bonds with good numerical stability, the time step should be carefully selected, and mostly it is a very small number in the scale of femtosecond.

In an all-atom (AA) MD simulation, if a large number of atoms and a longer simulation time are required, the large number of time steps to do time integration and particle interactions to calculate the force make the computation prohibitively challenging, despite the usage of techniques to reduce the number of interactions to consider, such as cut-off distance and link-list [54, 80]. To address this issue, the coarse grain (CG) technique is applied, which pays attention to a coarser resolution of the system rather than the atomic resolution. Consequently, the number of degrees of freedom can be reduced and a larger time step can be chosen to accelerate the simulation [91, 202].

A key point to note is that since the chain in a polymer network is very random and has many possibilities of conformation, accurate modeling should include all the possibilities, which however is impossible to do. Nonetheless, the use of MD simulations for modeling of polymer systems has been very successful, which is attributed to the ergodicity theorem which states that the time average equals to ensemble average. Therefore, material properties can be obtained from MD simulations using the dynamics of the system.

The application of MD simulations has enabled numerous novel insights and knowledge in the general field of mechanics, for example, the deformation mechanism of plasticity [27, 199, 76], the nanomechanical mechanism of strength, deformation, strength in spider silk [20, 21, 115], biomechanics of biological systems such as cells [148, 210], to name a few.

Overall, MD simulation is a feasible way to understand the multiphysics deformation mechanism of polymers [10]. For example, for cross-linked polymers, the degree of cross-linkages may be different, which classifies polymers into thermoplastics and thermosets. This intrinsic difference of cross-linkages grants distinct mechanical properties to them, which can be accurately captured by MD simulations [185, 64, 89].

3.2 Bridging MD simulation with a continuum model

A general rule to incorporate multiphysics mechanisms into the strain energy density function is to introduce new state variables associated with the new physics. The general expression of the total strain energy density is assumed additively as:

$$W(\boldsymbol{F}, \xi) = W_{\boldsymbol{F}}(\boldsymbol{F}) + W_{\xi}(\xi) \tag{14}$$

where $\boldsymbol{F}$ is the macroscopic deformation gradient, and ξ is the state variable for additional physics.

At the microscopic level, the macro-deformation $\boldsymbol{F}$ has to be connected to the chain-level kinematic state variables via affine deformation or nonaffine deformation assumption, which has been discussed previously. At the continuum level, this can be done by the second law of thermodynamics. For example, Hong et.al. developed a continuum model considering coupled diffusion and large deformation in polymer gels following the second law of thermodynamics principles by decomposing the total strain energy density into a stretching part and a mixing part without a coupling term [63].

In general, however, it is relatively unguaranteed that the complete decomposition is valid after introducing new physics. That is, it may involve a coupled term due to the coupling effect in nonlinear deformation [45], *viz.*, the new physics added may change the statistics of a polymer network. Therefore, to verify the assumptions or develop new models, it is important to study the microscopic deformation using molecular mechanics methods, such as MD simulations, which will be explained in detail by the following subsections and briefly by the representative examples in the next Section.

3.3 MD verification of affine deformation assumption

As discussed previously, the affine model assumes that all the junction points of a network are pinned to the elastic background, which is very strict. Thus, it would overestimate the elasticity when fluctuations of the junction points of a network are very strong. In that case, the phantom model seems to be a more appropriate choice. But the level of fluctuation the phantom model permits may not remain the same as the prediction of the model when states of the material system change, making the transition between phantom and affine models possible [2]. Therefore, it is not difficult to realize that the success of a continuum model relies on an accurate link from the microscopic evolution of the materials to the total strain energy density.

To demonstrate to which degree affine deformation assumption holds, two different polymer systems with distinctive chain lengths are prepared for MD simulations [98]. Specifically, the chain lengths are $N = 20$ for short chains and $N = 500$ for long chains, where N represents the polymerization degree. The systems are then subject to mechanical tests under uniaxial tensile, pure shear, and equal-biaxial tensile loading. The end-to-end distance change with respect to the first stretch invariant (I_1) is plotted in Fig. 3. For affine deformation, it would predict that $R_{ee}/R_{ee0} = \sqrt{I_1/3}$. As can be seen from Fig. 3, for systems with long chains, this assumption is satisfied very well; while for that with short chains, the true case deviates away from the assumption. Additionally, one can see that the affinity of the polymer network is loading-dependent. The affinity of polymer systems with longer chains is more susceptible to loading conditions.

From this simulation result, one can see that when the chain is short, the fluctuation of the junction points is not negligible, rendering the invalidity of affine deformation. On the contrary, for long chains, the affine deformation assumption suffices very well. In this example, molecular simulation provides an unambiguous quantification of the affinity.

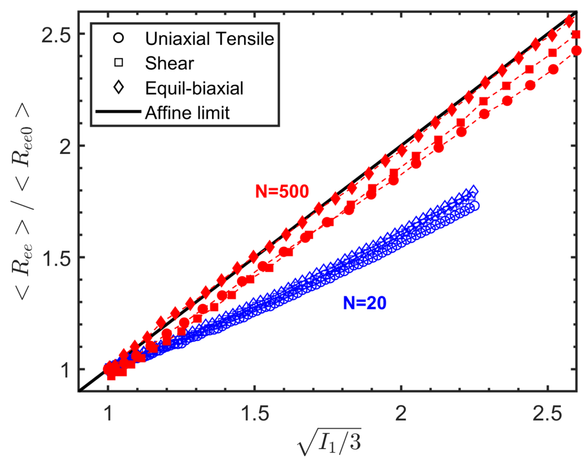

Fig. 3 Affinity of two polymer networks with chain length $N = 500$ and $N = 20$ under different loading conditions. Network with $N = 500$ follows the affine deformation, while network with $N = 20$ is described by phantom model.

3.4 MD simulation of polymer rheology

Material parameters from phenomenological models are usually obtained by curve fitting of experimental data. These material parameters have little to do with the intrinsic material composition and thus cannot guide materials design. With MD simulations, one can measure the material parameters of the polymer system of interest, which are connected to the polymer network composition. An example using MD simulations to calculate the polymer rheological properties is demonstrated here.

Viscous behavior of polymeric material is a major focus in polymer rheology [151]. The viscosity of polymeric materials has essentially two origins: the intrachain connectivity and inter-chain entanglements. The former dominates dynamics of the polymer chains by, *e.g.*, the diffusive Rouse model when the chains are short while the latter governs relaxation of the polymer chains when the chain length exceeds the critical entanglement chain length, making the inter-chain topological constraint significant [132]. Although the analytic solution to the Rouse model is available, it is nontrivial to understand the dynamics subject to entanglement. Polymeric materials with long chains share a great portion of industrially applied materials. Therefore, accurate examinations of the dynamics subject to entanglement are of great importance. The most successful model is the tube model originally proposed by de Gennes [38] and enriched by Doi and Edwards [40]. However, dynamics of the polymer chains deviates from the solution to tube model when factors like chemistry of constituents and polydispersity are considered [151]. Although efforts of carefully designed experiments have been devoted to gain a clear picture of the tube-like dynamics [151], molecular simulation plays a more significant role in terms of efficiency and cost. MD simulations can be used to study the tube-like dynamics by directly tracing details of the relaxation of polymer chains in melts [151].

Stephanou et.al. [151] applied MD simulations to calculate the rheological properties of polymer melts. The authors employed geometric-operation-based Z1 code [87] to analyze the microscopic dynamics of polymer chains, or the so-called primitive path analysis (PP analysis). The relaxation is quantified by tube survivability function directly estimated from trajectories generated by the MD simulations. The authentic relaxation behaviors are compared with predictions by a modified tube-like model, as shown in Fig. 4**a**. The discrepancy clearly suggests the limitations of the tube-like models in providing quantification of the chain dynamics even though they draw a conceptually appealing description. The tube survivability function from MD simulation corresponds to the prediction of double reptation model at the beginning but shows significantly faster relaxation over 1 nanosecond scale, which is attributed to the effect of constraint release (CR), the extra relaxation of the probed chain as a result of independent relaxation of the chain in the background. The insufficiency of the double reptation model is caused by its mean-field tube-like assumption about inter-chain topological entanglement although the assumption is the origin of the model's conceptual elegance. Estimation of zero-rate shear viscosity is compared with experimental data as shown in Fig. 4**b**. In addition, corresponding storage and loss moduli are compared with model predictions in Fig. 4**c** and Fig. 4**d**, respectively.

In this example, one can see that MD simulations can be used to characterize the rheological properties of polymer melts, such as viscosity, and the viscoelastic moduli. It's worthy of note that these material parameters are related to the chemistry and connectivity of polymers. As will be illustrated, these results are very helpful in developing a mechanistic continuum model of polymer viscoelasticity.

4 Representative Examples of Mechanistic-based Modeling of Polymers

4.1 Viscoelasticity of elastomers

Viscoelasticity is a significant mechanical property for elastomers undergoing large deformation, which is attributed to the diffusion process of the polymer chains [9, 59, 112, 163, 97, 216, 196, 197]. In a loading-unloading cycle, there is hysteresis in the stress-strain curve, rendering energy dissipation during the deformation process. There are many different approaches to develop a viscoelasticity model of elastomers, *e.g.*, see the summary in Refs. [216, 195] and references therein.

Here we present an earlier work from one of the authors, in which the viscoelasticity is decomposed into hyperelasticity, and viscosity from the polymer network [98]. The hyperelasticity originates from the

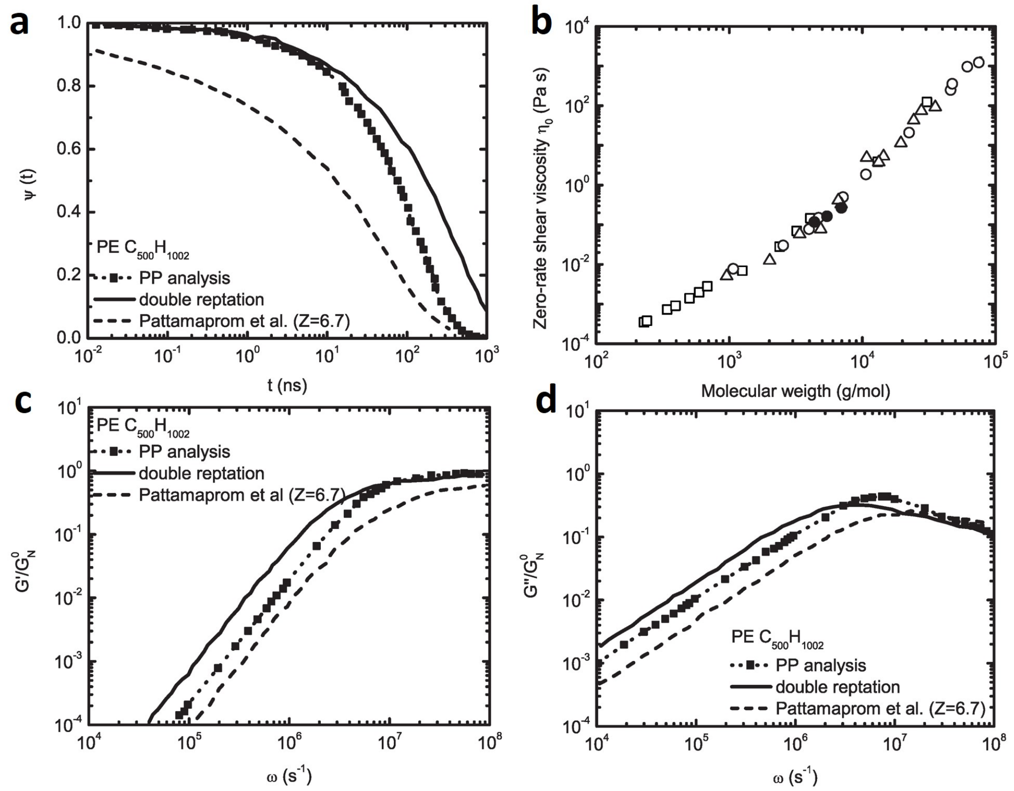

Fig. 4 Intrinsic relaxation dynamics studied by MD simulation. **a**: the tube survivability function estimation from simulation, compared with predictions of double reptation model and dual constraint model; **b**: zero-rate shear viscosity (the unfilled symbols are given by experiment); **c**: the storage modulus; **d**: the loss modulus. Theoretical results are drawn from data after Ref. [174, 109, 121, 122]. All figures are adapted from Ref. [151], copyright 2010 American Institute of Physics.

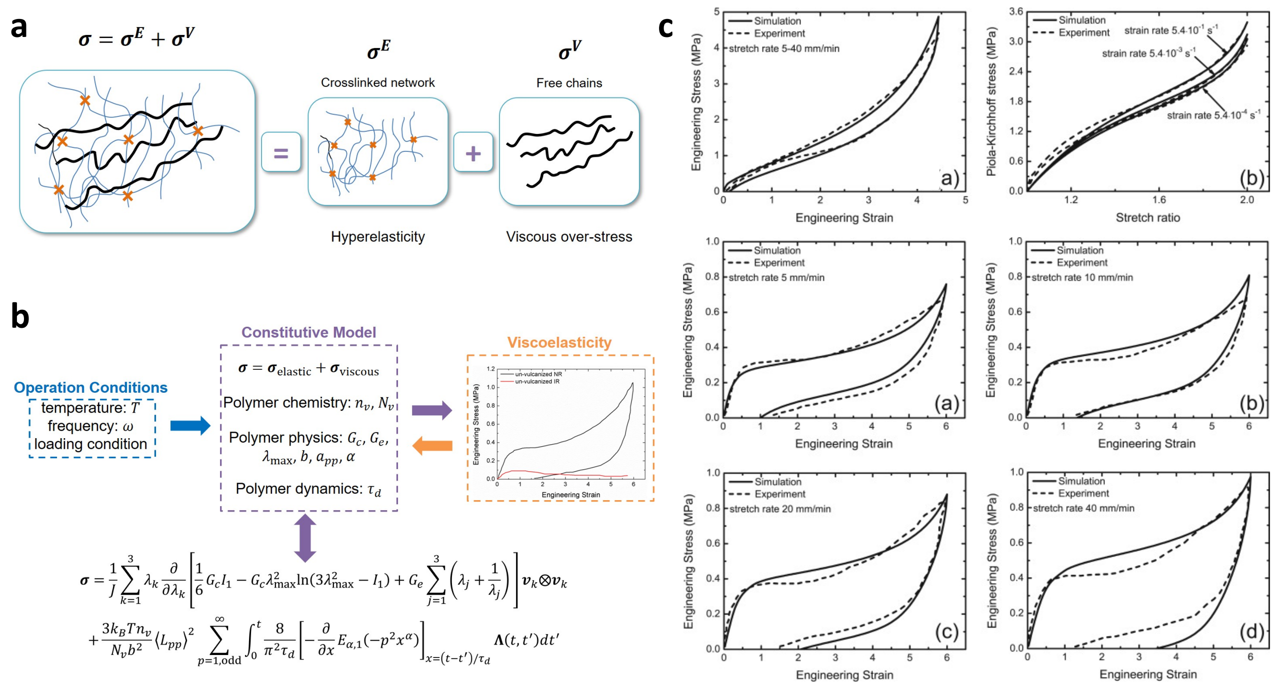

Fig. 5 Mechanistic modeling of finite viscoelasticity in elastomers. **a**: the illustrative decomposition of polymer networks into the cross-linked network and free chains; **b**: polymer chemistry, physics, and dynamics parameters in the constitutive model; **c**: performance of the model on several typical examples. All figures are adapted from Ref. [98], copyright 2016 Elsevier.

cross-linked network with entanglements, while the viscosity emerges from the diffusion of superimposed free chains. Fig. 5**a** demonstrates the schematic of this decomposition. The total true stress was assumed to be the summation of the hyperelastic stress and the viscous stress, as shown in Fig. 5**b**. For the hyperelasticity, the Davidson-Goulbourne model was applied to capture the nonlinear deformation behaviors induced by cross-linkages and entanglements, as verified by MD simulations. For the viscous stress, a modified reptation model was proposed to capture the viscous forces, since the classical one does not account for the energy dissipation in a finite strain very well [40]. This modification was further confirmed by MD simulations [98].

The diffusion of free chains was described by the tube model of reptation motion due to uncrossability constraints of neighboring chains. In large deformation, however, this model does not work well since in the original model, the tube diameter and the primitive chain (the center axis of the tube) length were constant while it actually changes in large deformation [154, 126, 118]. In addition to these two modifications, it further considered the change of chain orientations and fractional order viscoelasticity. All these modifications were confirmed by MD simulations. So that the modified tube model can model finite strain viscous stresses as shown in Fig. 5**b**. The details can be referred to in the original paper [98]. The predictions were then made on both unvulcanized and vulcanized natural rubber and compared with experimental data, as shown in Fig. 5**c**. It can be seen that the model can capture the strain-rate dependence, strain hardening, and strain softening effects qualitatively well.

Last but not least, it is worthy of note that when fillers, such as carbon black and silica, are added into the elastomer matrix (see Fig. 1), the mechanical properties especially the inelasticity can be significantly improved [163, 35, 95]. Besides the reinforcement effects and viscoelasticity, the anisotropic effect, Mullins effect, hysteresis, and permanent set have been widely studied in filled elastomers [44, 111, 127, 81, 35, 124], while few models are mechanistic-based and can model all these phenomena simultaneously. A mechanistic-based multiscale model incorporating chain level mechanism remains to be developed for filled elastomers [178].

4.2 Thermomechanical-coupled viscoplasticity in polymers

For many polymers, the chains are randomly oriented and thus they are named amorphous polymers. In some cases, the polymer chains can be partially aligned and folded to form ordered regions called lamellae or crystallite. This process is called crystallization, which can be induced by cooling from a melting state [194, 86], stretching [105, 110] or solvent evaporation [160, 96]. Crystallites, considered as physical cross-links [144], can significantly change the mechanical behaviors of polymers [123, 13, 108, 144], such as on the yield stress [66], and the disentanglement [209].

In a work by Bouvard et. al. [11], MD-guided hierarchical multiscale modeling was applied to the thermomechanical-coupled viscoplastic modeling of polymers. The stress-strain curve obtained by MD simulation is shown in Fig. 6**a**, which captured the elastic regime, yield, strain softening, and strain hardening regime. Based on the MD results, they proposed three physics-based internal state variables (ISV) to model the viscoplasticity of polymers [12]. The first strain-like scalar $\bar{\xi}_1$ is to capture chain entanglement slippage which causes strain softening. The second strain-like scalar $\bar{\xi}_2$ is to capture the strain hardening induced by chain alignment and coiling at a large strain state. And the last strain-like tensor $\bar{\boldsymbol{E}}^{\bar{\beta}}$ captures the strain hardening induced by chain stretching. The evolutions of the material parameters were monitored by MD simulations, as shown in Fig. 6**a**. The material constants were also calibrated using MD simulations. Therefore, the plastic flow and hardening law can be informed from these MD simulations. This model was shown to be able to capture temperature effect, strain-rate dependence, and stress-state dependence in the polymers.

At the continuum level, the decomposition of the deformation gradient is carried out to deal with elasticity, rate-dependent plasticity, and thermal component, as depicted in Fig. 6**b**. The comparison between the model prediction and experimental tests at different temperatures and loading rates is shown in Fig. 6**c**. One can see that the model can capture the typical mechanical behaviors, such as strain softening and strain hardening, very well.

4.3 Self-healing polymers

Self-healing polymers have been revolutionizing the man-made engineering society via bringing in the autonomous intelligence that widely exists in nature. They have been applied to a wide range of engineering applications, including flexible electronics [167], energy storage [177], biomaterials [18], and robotics [168]. Motivated by these applications, various self-healing polymers have been synthesized during the past years [201, 186, 169, 193]. They typically fall into two categories. The first category is “extrinsic self-healing” that harnesses encapsulates of curing agents [188, 170]. The second category is “intrinsic self-healing” that harnesses dynamic bonds, such as dynamic covalent bonds [24, 53, 69, 107], hydrogen bonds [31, 25], and ionic bonds [182, 157]. The dynamic bonds can autonomously reform after fractures or dissociations. Here we primarily focus on the second category.

Despite the success in syntheses and applications, the theoretical understanding of self-healing polymers

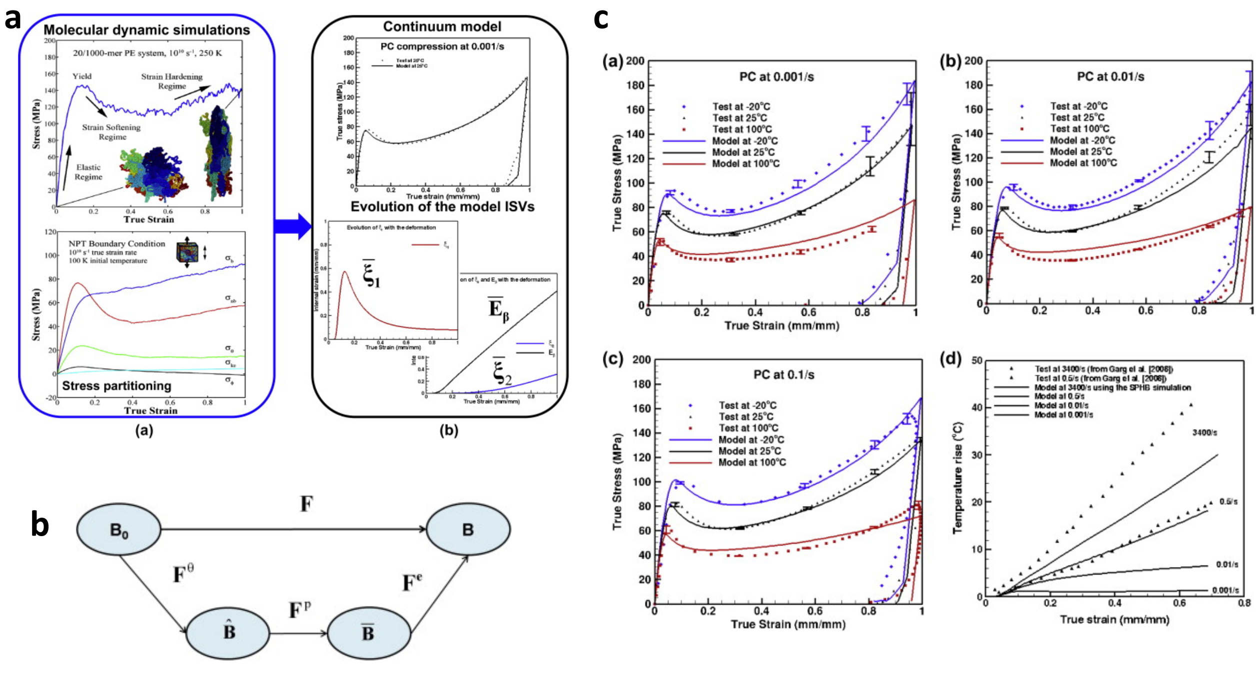

Fig. 6 Mechanistic modeling of finite viscoplasticity in polymers. **a**: the multiscale illustration of molecular-dynamics-simulations informed continuum model development; **b**: the decomposition of the macroscopic deformation gradient to account for thermally coupled viscoplasticity; **c**: performance of the continuum model compared to experimental tests on polycarbonate. All figures are adapted from Ref. [11], copyright 2012 Elsevier.

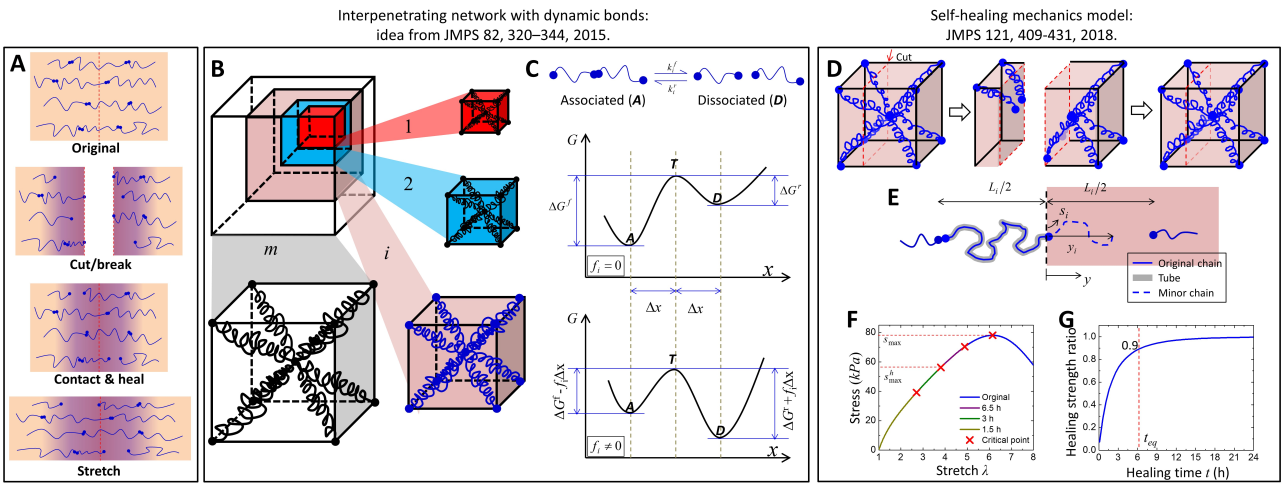

Fig. 7 Mechanistic modeling of self-healing polymers. **a**: Healing process. **b**: Interpenetration network model. **c**: Bell-like model for a dynamic bond. **d**: Conceptual self-healing model. **e**: Diffusion and binding of a polymer chain. **f**: Predicted stress-stretch behaviors of original and self-healed polymers. **g**: Predicted relation between the healing strength ratio and healing time. All figures are adapted from Ref. [204], copyright 2018 Elsevier.

has left behind [201]. Back in the 1980s, scaling models were proposed for the interpenetration of polymer melts [191, 192]. After entering the 21st century, MD simulations were employed to understand the healing behaviors of polymers [155, 5, 214, 47]. It remains long-term overdue how to analytically model the interfacial healing of self-healing polymers. The missing of this theoretical understanding would significantly drag down the innovation of self-healing polymers to achieve optimal healing performance.

Recently, Wang *et al.* have developed a series of theoretical models to understand the self-healing mechanics of soft polymer networks [179, 180, 204, 205, 198]. They consider the healing process of a polymer network linked by dynamic bonds shown in Fig. 7**a**. The polymer is cut into two parts and then contact back. After a period of healing time, the sample is stretched until rupture. The self-healed sample is composed of two segments (Fig. 7**a**): a small "self-healed segment" with re-bridged polymer chains (purple) and two "virgin segments" with intact polymer networks (light pink). The modeling effort is devoted to theoretically quantifying the relationship between the healing percentage and the healing time. The healing percentage is indicated by the ratio between the tensile strengths of the healed and the original samples [201, 186, 169, 193, 55].

To theoretically model the interfacial healing of self-healing polymers cross-linked by dynamic bonds, two technical challenges need to be addressed: (1) how to understand the mechanics of dynamic-bond-linked polymer networks, and (2) how to understand the network evolution during the healing process. To address the first challenge, an interpenetrating network model is employed to consider many types of networks that interpenetrate each other in the material space (Fig. 7**b**) [181]. Each type of network is composed of polymer chains of the same length and linked by dynamic bonds, similar to the covalently cross-linked polymer networks. The chain-lengths among different networks follow an inhomogeneous statistic distribution. Under stretch, dynamic bonds obey force-dependent chemical kinetics to transform between the associated state and the dissociated state (Fig. 7**c**). The force-dependent chemical kinetics can be described by a Bell-like model [7]. To address the second challenge, the healing process is considered as a coupled behavior of inter-diffusion of dissociated chains and re-binding of dissociated dynamic bonds (Fig. 7**d-e**). The curvilinear motion of the polymer chain can be explained by a reptation-like model [38, 39], and the binding kinetics by the Bell-like model [7]; therefore, the interpenetration of the polymer chain across the fracture interface can be modeled as a diffusion-reaction system [180, 204], which has been recently confirmed by large-scale MD simulations [147]. After addressing the above two challenges, stress-strain behaviors of the original and the healed self-healing polymers can be theoretically calculated (Fig. 7**f**). As the applied stretch increases, more and more dynamic bonds are dissociated, and the corresponding stress increases and then decreases. The maximal stress (tensile strength) is corresponding to the material rupture. With increasing healing time, the tensile strength of the healed polymer increases until reaching a plateau that is the tensile strength of the original polymer. In this way, the relationship between the healing percentage (healed/original strength) and the healing time is calculated (Fig. 7**g**). The theory can be used to explain the self-healing behaviors of polymers cross-linked by various dynamic bonds, such as dynamic covalent bonds [69, 107, 203, 67], hydrogen bonds [31], and ionic bonds [157, 67].

4.4 Another mechanistic modeling of multifunctional polymers

Electroelasticity in polymers. Electro-active polymers (EAPs) are soft elastomers coated with electrodes, which are sensitive to the external electric fields with significant size and shape changes. They have found wide applications such as polymeric transducers [46, 128] and polymeric actuators [183]. Continuum mechanics theory has been well developed to account for the electromechanical coupling of this material [42, 43, 101, 159, 158]. In recent years, several works have been done based on molecular chain statistics, which are connected to the continuum models [28, 70]. The work worthy of note by Cohen et.al. considered the change of statistics of polymer chains under electric fields and derived new formulations for electroelasticity [28, 29], which can serve as references for further MD simulations to study the validity of the theories as MD-based studies are very few on this topic.

Magnetoelasticity in polymers. The magneto-responsive polymers are usually designed by adding hard or soft magnetic composites into the polymer matrix (*e.g.* elastomers) [6]. Under the influence of external magnetic fields, these materials demonstrate significant magnetoelastic behavior. They have been designed to work as soft actuators [37, 149], and soft robotics [65, 3]. Continuum mechanics theories have been formulated very well to understand and design these materials [15, 41, 141, 213]. In addition, MD simulations have been extensively applied to study chain-level statistics and dynamics under the influence of magnetic forces [136, 137, 131, 139]. In the near future, we expect that these MD simulations and continuum models can be well integrated together to formulate mechanistic-based models for these magnetorheological elastomers [51].

Hydrogels. A hydrogel is a type of cross-linked polymers which have rich hydrophilic structures that can contain a large number of water molecules within the polymer network [1, 156, 211]. Due to the similarities (soft and wet) and thereby the compatibility between hydrogels and biological tissues, they have emerged as a very promising material for bioelectronics devices [57, 207], and ionotronics devices [200, 176]. Continuum-level mechanics theory has been developed to account for the mechanical behaviors of polymeric gels and hydrogels [63, 22, 104]. On the molecular level, MD simulations have also widely applied to study the structure and dynamics of hydrogels [161, 162, 26, 175]. However, the connections between MD studies and the continuum modeling of hydrogels have not been extensively investigated [88].

Liquid crystal polymers. Liquid crystal polymers (LCPs) are a kind of polymers with sufficient rigid rodlike monomers (also known as mesogens) as either side groups or incorporated in the backbone chains [73, 72, 132]. Due to the extremely unreactive and inert features, they have exceptional properties, such as chemical resistance, heat resistance, and electrical resistance [140, 77]. Additionally, for its light-sensitive feature, they have been used for light-activated actuators and soft robotics [119, 103, 32]. Mechanically, they demonstrate significant anisotropy in deformation because of the intermediate state order between crystalline solids and amorphous liquids [132], and also because of the phase transitions between the nematic phase and the smectic phase [189]. Continuum level modeling has been extensively carried out [30, 172, 79]. MD simulations have also been applied to study LCPs [120, 19, 152, 190]. However, mechanistic-based studies are still very limited, which calls for further studies.

5 Summary and Outlook

Polymers are long-chain organic molecules. Their mechanical behaviors are dominated by configurational entropy changes. Additionally, the introduction of additional active elements into the polymer networks makes their mechanical behaviors even more complicated. The conventional way to deal with this coupled problem is to decompose the multiphysics responses into single components and consider the entire response as the summation of the decoupled elements. For instance, the mechanical response of hydrogels can be decomposed into two parts: the swelling of the polymer network and mixing between polymer chains and solvents [63].

In this work, we demonstrated that molecular simulations can be very useful to study the intrinsic deformation mechanisms of polymer chains and networks in the multiphysics context. Taking advantage of MD simulations, the contributions of each component in polymeric materials and their evolution can be explicitly quantified. Thus, molecular simulations can link the polymer network deformation and continuum model across scales, leading to the formulation of a physics-informed continuum model. It can also serve as an effective way to verify the assumptions made in the continuum models, and study the applicable ranges of these models. Namely, it can be used as virtual experiments to check the validity of the direct decomposition made for a multiphysics problem. By highlight several examples in mechanistic modeling of multifunctional polymers, this concept and philosophy have been further elucidated.

However, there are still scientific challenges and limitations, which are mainly summarized as follows:

(i) Despite simple, direct decomposition of multiphysics mechanisms into single components might introduce potential issues since it neglects the coupling effects without explicitly considering the applicable range of the decomposition. It could be valid in a certain range, such as small deformation, but maybe not in other situations. For example, under strongly coupled conditions involving material instabilities, these interactions may not be easily decomposed. In addition, the scale effect can also make the coupling effect more intricate, since the coupling effect might be scale-dependent [114].

(ii) The statistical mechanics of polymer networks assumes perfect network, while real polymer system contains significant defects, such as loops and dangling chains [60] which have little contribution to the polymer elasticity. How to account for defects using statistical mechanics and molecular mechanics modeling is a challenge. Recently, Zhong et. al. combined experiments and simulations to study the influence of loops on hydrogel elasticity [215]. They developed a theoretical model of polymer elasticity (shear elastic modulus) on the loop fractions, which was validated by Monte Carlo simulations very well. This work provided a good reference to address this challenge.

(iii) Real polymer systems are synthesized by polymerization, which usually results in nonuniform polymer chain-length distributions, so-called polydispersed polymer systems. How to account for the influence of chain-length distributions on polymer elasticity is a challenge. There are several recent efforts on this problem. Wang et. al. considered five different chain-length distributions (Dirac Delta, uniform, normal, log-normal, and Weibull distribution) and combined them with the Arruda-Boyce model to derive the polymer elasticity model [181]. Their results showed that the difference in the stress-strain curve under these five distributions is very small for stretch ratio in the range of $1 \sim 3$, compared to experiments. Itskov and Knyazeva studied the dependence of rubber elasticity and softening on chain-length distributions (geometric probability density function) [71]. Later, Verron and Gros developed a theory for polymer elasticity considering arbitrary chain-length distributions under the equal force assumption in the polymer networks [173]. Despite these efforts, theoretical work is still needed. Research questions include: which chain-length distribution is more consistent with real systems? Do all kinds of polymers share the same chain-length distributions? Do chain-growth polymerization and step-growth polymerization give the same chain-length distributions? How much influence does chain-length distribution have on polymer elasticity and viscoelasticity?

(iv) It is a challenge when polymer systems undergo extremely large deformation and even fracture. Very recently, Lin and Zhao developed a theoretical model to shed light on the influence of polymer defects on the fracture of the polymer system [99]. They showed that these defects toughen the polymer network while weakening the polymer network at the same time. These competing effects depend on the densities and types of defects. The theoretical results were validated well with experiments. However, it remains to be further explored and quantified from molecular simulations.

(v) Despite its effectiveness, MD simulation has built-in limitations in polymer modeling. It is not surprising that a molecular model with hundreds of thousands or millions of degrees of freedom is usually necessary for accurate sampling of the microscopic properties of interests. As a result, the computational cost of molecular simulation could be sometimes intimidating, leading to an intrinsic tempo-spatial limitation, which is usually around hundreds of nanometers and nanoseconds respectively, for the all-atomic model. It would be very difficult for long-time dynamics simulations, like reptation of long linear polymer chains in the melt. Although coarse-grained models are widely used, attempting to circumvent the tempo-spatial limitation, its deficiency is the inevitable entropic changes of the system, resulting in altered structural or dynamics properties. Special care is needed in order to compensate for the side-effect, which remains a challenge to be addressed [202].

In summary, we discussed how to formulate the molecular simulation-guided and physics-informed mechanistic models for multifunctional polymers. A physics-based continuum model, with material parameters related to the molecular and microstructures, can dramatically facilitate the design of multifunctional polymers to meet the high demand of soft materials in numerous fields, especially on (i) using this mechanistic framework to address the aforementioned challenges, as there are usually assumptions made in developing theoretical models. Thus, it is very helpful to apply this mechanistic method to study the real polymer systems with defects, chain-length distributions, and fractures. (ii) Recently, data-driven computational techniques are emerging to predict the complex mechanical behaviors of materials without explicit constitutive modeling [166, 164, 165, 135]. These data-driven methods also open a promising avenue to directly use the molecular information of polymer chains and networks, *e.g.* configurations of chains, for predicting their mechanical behaviors [52]. Therefore, using MD simulations as numerical experiments and combined with data-driven methods, novel constitutive relations may be discovered. We anticipate that this work can provide some useful insights in mechanistic modeling of polymers, and inspire future studies in the near future.

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