Invited Paper

DFT-MD-CM combined multiscale mechanics on the opto-mechanical behavior of polymer network

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ABSTRACT

To obtain comprehensive understanding about the behavior of photo-responsive polymer network, wherein light irradiation, macromolecular motion, and large-scaled deformation are intimately entangled, a multiscale investigation to the opto-mechanics is strongly called. In this work, we present a multiscale-based framework for the smart polymer network under light and thermal stimuli, which encompasses quantum mechanics, molecular dynamics, and continuum mechanics. Distinctive physics in each scales, such as photon-stimulated E-Z isomerization, configurational symmetry change, and macroscopic phase behavior are investigated via separated mechanics, later incorporated into the multiscale framework; as a results, light induced motions of acrylate-based nematic polymer are simulated which agree well with the experimental reports.

1. INTRODUCTION

Opto-mechanical behavior broadly refers a light-induced macroscopic manipulation found in liquid crystalline polymer network incorporating photochromic chromophore such as azobenzene (Finkelmann 2001). As such photo-responsiveness does not require external wirings and power systems unlike existing smart materials, the behavior has been deemed as an attractive measure for remote controlled wireless actuators and sensors.

Behind the behavior are several physical traits: photon induced E-Z isomerization (i.e. geometric isomerization), molecular conformation and its symmetry, and macroscopic motion by which generates macroscopic motion to moderate photostrain. Multiscale consideration accompanied by multiphysical understanding is therefore required to both simulate and design opto-mechanical motions.

In the present work, we propose sequential multiscale schematics that bridges different physics found in the opto-mechanics. As an analogy to opto-mechanical behavior, wherein isomerization ratio determined by light irradiation condition changes thermotropic phase behavior of the molecule conformation and subsequent macroscopic behavior, quantum mechanics based on density functional theory (DFT),

molecular dynamics (MD) are incorporated into classical continuum modeling (CM). These coupling not only enhances our knowledge about photo-responsive polymer (PRP), but also renders the material as user-comprehensible one for novel smart systems.

2. DFT-MD-CM coupled multiscale

Schematic illustration of multiscale framework of PRP structure is shown in the Fig. 1. The information of each scale (right box), such as position, isomerization ratio n_{cis}, and changed microstate are flow from upper to bottom as indicated by an arrow.
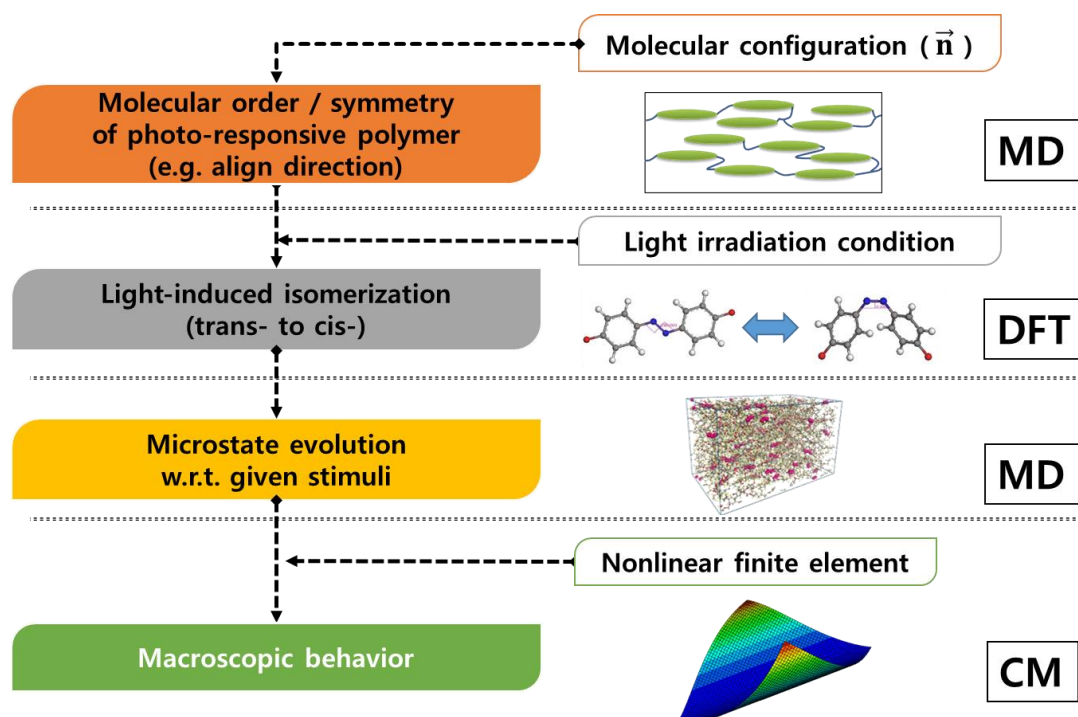

Fig 1. Schematic illustration of information flow in proposed multiscale simulation. Quantum mechanics (DFT), molecular dynamics (MD) and continuum-scaled computation (CM) are cooperating with one another, which results to the relation between macroscopic deformation and the light irradiated onto the surface.

In the lowest scale, we execute DFT simulation in order to achieve light-induced stimulation of the chromophores, which determines whether the molecule isomerizes or not; in specific, a stimulate Raman adiabatic passage (STIRAP) method cooperating with nonlinear Beer's law determines an isomerization ratio, for given intensity and polarization angle of actinic light. The microscale consideration, on the other hand, is simulated via MD. Firstly, the molecular conformation of the PRP is obtained via energetically relaxing the nematic cell with uniaxial alignment. MD simulation also investigates the thermotropic behavior of the PRP for given *cis-* population found in the unit cell; an effect of the temperature and geometric distortion to the deformation of the cell is thus elucidated. The simulation techniques are largely in debt to the reference

(Choi 2015) and the aid of conjugate gradient module embedded within LAMMPS, an open-source molecular dynamics simulation program. Lastly, CM computes the behavior of the polymer network accompanied by the microscopic changes induced by external stimuli.

2.1 STIRAP and the light decay within the cell

A time dependent Schrodinger equations with regards to transition between states marked by densities of state ρ_{jj} and ratio of transitions ρ_{jk}, are presented in Eqn. 1.

$$\frac{d\rho_{jj}}{dt} + \left(k_j + \gamma_j\right)\rho_{jj} - \sum_p \left(k_{pj} + \gamma_{pj}\right)\rho_{pp} = \frac{i}{\hbar}\left[\sum_n V_{nj}\rho_{jn} - V_{jn}\rho_{nj}\right]$$

$$\frac{d\rho_{jk}}{dt} + \left(k_k + \gamma_j + i\omega_{jk}\right)\rho_{jk} = \frac{i}{\hbar}\left[\sum_n V_{nk}\rho_{jn} - V_{jn}\rho_{nj}\right] \quad (1)$$

$$V_{mn} = -\varepsilon \cdot d_{mn} = -\left(\varepsilon_o \cos\left(\omega_{mn}t\right)\right)\cdot d_{mn}$$

Where ε is voltage vector of light, ω is an angular momentum of light, and γ, k are representing spontaneous degradation ratio and absorption ratio. By coupling light-induced isomerization probability from STIRAP calculation with nonlinear Beer's law, overall profile about distribution of *cis-* state molecules are computed.

2.2 Molecular dynamics simulation

Microstate change (e.g. molecular conformation shape) with respect to induced phase transition between *trans-* and *cis-* are analyzed via molecular scaled *in-silico* simulations. Fig. 2 illustrates a shape change between *trans-* state and *cis-* state molecular model of azodye portion of the chromophore. Significant geometric change is observed in length between oxygen-oxygen (atoms at either end of the molecule) and dihedral angle of N=N bonds.
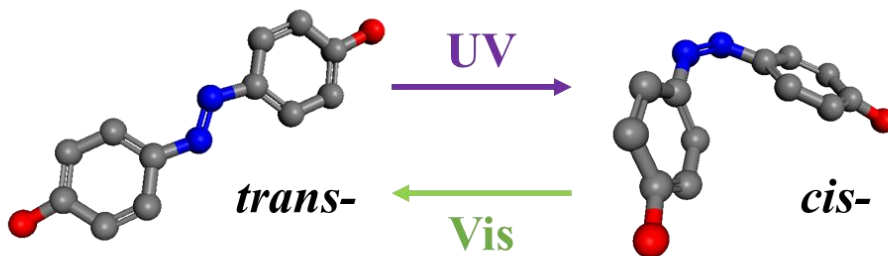

Fig. 2 Illustration of geometric shape for each *trans-* and *cis-* molecule; E-Z isomerization reversibly occurs due to light irradiation with different wavelength.

To introduce such chemical aspect into the classical MD, light-reactive potential is employed with minor modification that reflects DFT calculation. Although it truncates complex photon-atom interactions significantly, such adoption yields promising implications about surface-modulation and thermodynamic properties of phase transition. For the computation of the latter properties, we carry out heating-up simulation with different n_{cis} that correspond to different actinic light conditions as demonstrated by Fig. 3; the collapsing order of rod molecules becomes more abrupt near transition temperature, as we increase the *cis-* population within the cell. Detailed simulations and results can be found in the reference (Choi 2015).
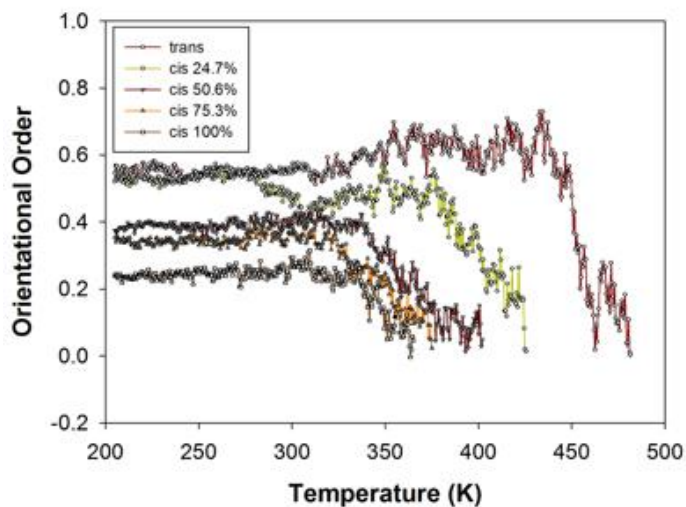

Fig. 3 Orientational order profile of the liquid crystal network model with different *cis-* state population

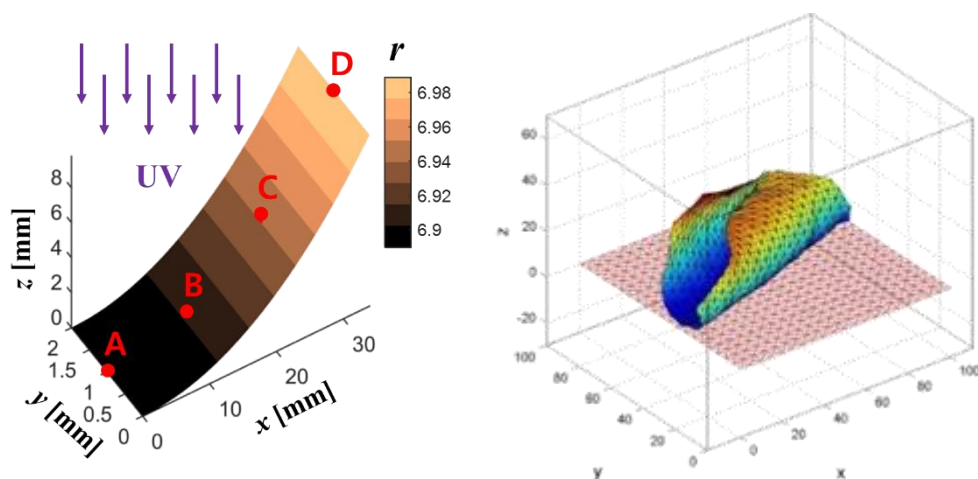### 2.3 Classical continuum mechanical description

Fig. 4 (Left) thin strip deformation induced by uniaxial alignment along x direction (Right) a tilted bending of square PRP sheet, generated by polydomain of which monodomain constituent is randomly aligned.

The aforementioned relationship between changing orientational order that is stimulated by light irradiation, and the spontaneous shrinkage of the unit cell is introduced into classical continuum mechanical description. A bending behavior of the PRP, by which light-induced manipulations are distinguished from thermal-induced uniaxial shrinkage is simulated as shown in the Fig. 4. Although the deformation of each element is small, we considered geometric nonlinearity to include rigid-body rotation of the element by employment of element-independent corotational (EICR) formulation. EICR formulation, in which pre- and post- processing that separate rigid body motion from total displacement, is especially beneficial to the multiscale formula adopted herein, as the consideration of material nonlinearity is yet to be provided.

3. DISCUSSIONS

In this work, we present multiscale method that provides the nonlinear relationship which couples light irradiation and macroscopic deformations, an interesting characteristic of the PRP. Opto-mechanical properties behind such behaviour is analysed by scale deconvolution, which ranges from a density-functional theory (DFT) that computes probability of E-Z isomerization for given actinic light, a molecular dynamics (MD) that considers microscopic state evolution with changes of the molecular conformation, and classical continuum mechanics (CM) that computes macroscopic structural behaviour by combining the information from the lower scales (i.e. DFT and MD).

With this work, the authors envisages not only a deeper understanding about the PRP and its opto-mechanical behavior, but also efficient design towards a novel light-responsive smart system that are driven by light, which is full of possibilities in near future.

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