중앙대학교 세포화학동력학 창의연구단

개단식 및 기념 심포지엄

일시: 2017년 01월 23일(월) - 24일(화)

장소: 중앙대학교 서울캠퍼스 310관 B5 502호

CDLC Creative Research Initiative
Center for Chemical Dynamics in Living Cells
National Research Foundation of Korea

◈ 오시는 길

<중앙대학교 서울 캠퍼스 맵>

프로그램

2017 년 1 월 23 일 (월)

세포화학동력학 창의연구단 개단식	
11:00-12:30	환영사: **공광훈 자연과학대학장 (중앙대)** 축사: **이상엽 교수 (서울대), 조민행 교수 (고려대)** 연구단 소개: **성재영 교수 (중앙대)**
12:30-14:00 Lunch	중앙대학교 102 관 R&D center 11 층 University club
기념 강연 I: 좌장 황현석 교수 (강원대)	
14:00-17:50 Session1	**14:00 - 14:50 이상엽 교수 (서울대)** Perspectives on the Diffusion-Influenced Bimolecular Reaction Kinetics **15:00 - 15:50 성우경 교수 (포항공대)** Surmounting the "Insurmountable" in Biophysical/Chemical Complexes **16:00 - 16:50 심은지 교수 (연세대)** Consistency in Density Functional Calculations **17:00 – 17:50 정연준 교수 (서울대)** Introduction to Statistical Mechanics of Phase Transitions
18:00	저녁식사 및 연회

2017 년 1 월 24 일 (화)

기념 강연 II: 좌장 은창선 교수 (한국외대)	
09:00-09:50	**성봉준 교수 (서강대)** A (Brief) Introduction to Challenges in Molecular Simulations for Polymeric Systems: Microfibers and Loop Formation Kinetics as examples
10:00-10:50	**전재형 교수 (포항공대)** Quantifying Anomalous Transport in Living Cells: From Subdiffusion to Superdiffusion
11:00-11:50	**조정효 교수 (포항공대)** Scaling Law for Irreducible Entropy Production in Critical Systems
12:00-12:50	**김지현 교수 (중앙대)** Chemical Fluctuation Theorem for Stochastic Gene Expression
12:50-14:30	점심식사: 중앙대학교 310 관 B4 참마루 식당

구두 발표: 좌장 한승수 교수 (중앙대)	
14:30-14:50	**박윤재 (서강대)** Translational and Rotational Decoupling Using Tracers of Locally Favorable Structures in Glass-Forming Liquids
14:50-15:10	**송수환 (연세대)** How to Obtain Accurate Adiabatic Energy Gap of Transition Metal Complexes
15:10-15:30	**이준열 (광운대)** Prediction of Chlorosulfolipid (Danicalipin A) Membrane Structure Using Combined Coarse-Grained and Atomistic Model Simulations
15:30-15:40	**Coffee break**
15:40-16:00	**노찬우 (서울대)** Study of Glassy Systems with Both Static and Dynamic Interactions in the Trajectory Space
16:00-16:20	**정인춘 (중앙대)** Chemical Fluctuation and Reaction Dynamics of Single Enzymes at Mesoscopic Concentrations
포스터 발표	
16:30-18:00	**Poster Session**

Abstract

(1 월 23 일)

Perspectives on the Diffusion-Influenced Bimolecular Reaction Kinetics

Sangyoub Lee

Department of Chemistry, Seoul National University, Seoul 08826, South Korea

E-mail: sangyoub@snu.ac.kr

Since the seminal work of Smoluchowski, the theory of diffusion-influenced bimolecular reactions has been refined and generalized in many aspects [1-3]. The solution of Smoluchowski equation with various boundary conditions and/or reaction sink functions, which models the coupling of transport and reaction, has been sought by using various mathematical techniques. Various factors affecting the reaction kinetics, such as the reversibility of reactions [3-5], high reactant concentrations [1,5-7], inertial motion of the reactants [8,9], disordered media resulting in sub-diffusive motions [10,11], and so on, have also been investigated. Although mainly formal, the whole events of reaction and transport have also been examined starting from the molecular levels [9,12,13]. In this talk, I will describe some contributions from our group to this old but still fascinating research field.

References

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Surmounting the "Insurmountable" in Biophysical/Chemical Complexes

Wokyung Sung

Department of Physics, POSTECH, & IBS, Center for Self-Assembly and Complexity

E-mail: wsung@postech.ac.kr

Due to structural connectivity and flexibility, some biophysical/chemical complexes, such as polymers, membranes and many other self-assembled structures, manifest a host of interesting cooperative phenomena. Nature utilizes the ambient fluctuations to enable such matter to cross over seemingly insurmountable barriers for self-organization. After introducing the basic physical features of such complexes and the environments, I will present how the fluctuations play the key roles, by sketching the examples we studied. In particular I will focus on our recent problems, the bubble-induced short DNA bending and looping [1-3] and the vacancy-induced self-assembly to the recently-synthetized naoncapsules[4-6].

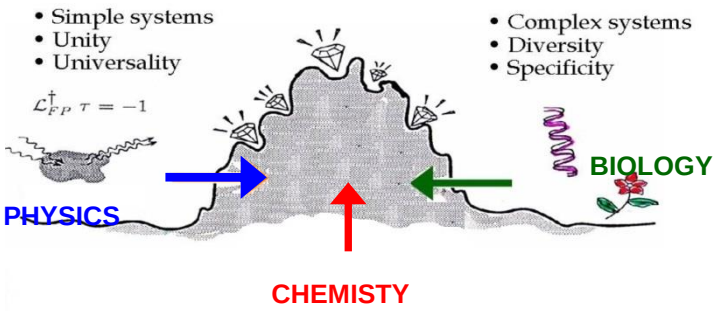

Fig. 1 Crossrods between biology, chemistry, and physics

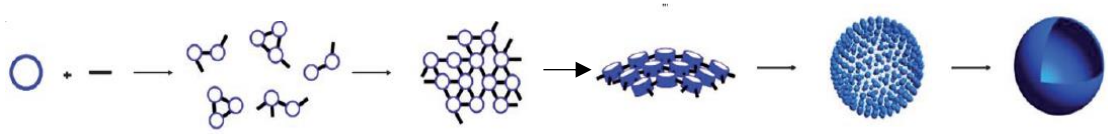

Fig. 1 Moleculae self-assembly to a nanocapsule

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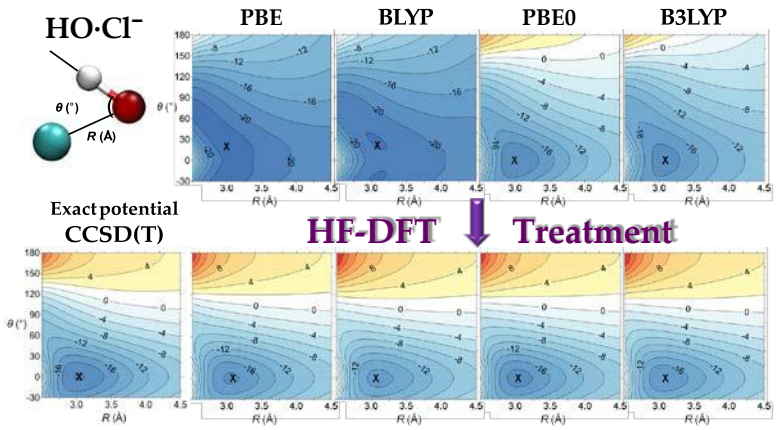
Consistency in Density Functional Calculations

Eunji Sim*

Department of Chemistry, Yonsei University, Seoul 03722, Korea

E-mail: esim@yonsei.ac.kr

There remain challenges where density functional theory (DFT) suffers from the self-interaction error. We show that the energy error of any variational density functional calculation can be decomposed into errors contributed from the approximate functional and that from the self-consistent Kohn-Sham density [1]. In vast majority of DFT calculations, the functional error dominates: however, we have found several abnormal cases where the density-driven error dominates. In particular, any self-interaction error can be decomposed this way and some of them turned out to be density-driven. We suggest a simple cure for these abnormal calculations, density corrected density functional theory (DC-DFT). DC-DFT is a non-variational DFT which uses more accurate density than the self-consistent approximate density. One of the simplest ways to implement the method is to use the Hartree-Fock density, i.e., HF-DFT, which has been already known to give remarkably accurate results in some cases. We also found that a small HOMO-LUMO gap in DFT calculations leads to large density-driven errors and, thus, may be used as an indicator of abnormal calculations. We discuss examples including simple two electron atom energies [1], electron affinities of small molecules [2], dissociation curves [3], and preferred geometries of ions and radicals in solution [4], transition metal complexes, and more. In addition, the importance of being self-consistent in DFT is discussed.[5]



Fi g. 1 Improvement using HF-DFT: Potential Energy Surface of $HOCl^-$.
(top panel) self-consistent DFT results and (bottom panel) exact and HF-DFT results

References

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Introduction to Statistical Mechanics of Phase Transitions

YounJoon Jung*

Department of Chemistry, Seoul National University, Seoul 08826, Korea

E-mail: yjjung@snu.ar

In this tutorial lecture, I will give a brief introduction to statistical mechanical theory of phase transitions. The lecture is far from being either extensive or exhaustive in terms of its coverage on the vast area of phase transitions. Rather, I will focus on a simple theoretical model, that is, Ising model, which is simple enough to allow for an exact solutions in lower dimensions, yet complex enough to exhibit non-trivial behaviors at higher dimensions. Using the model system, I will illustrate some imporant concepts such as order parameter, spontaneous symmetry breaking, mean-field theory, Monte Carlo simulation, umbrella sampling method, and idea of renormalization. If time permits, I will talk about our recent study on the statistical mechanics in trajectory space based on non-equilibrum ensemble methods.

References

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Abstract

(1 월 24 일 오전)

A (Brief) Introduction to Challenges in Molecular Simulations for Polymeric Systems: Microfibers and Loop Formation Kinetics as examples

SeulKi Kwon, Hyun Woo Cho and Bong June Sung*

Department of Chemistry, Sogang University, Seoul 121-742, Korea

E-mail: bjsung@sogang.ac.kr

Molecular simulations (including molecular dynamics simulations and Monte Carlo simulations) have been used extensively to investigate various physical and chemical properties of polymeric systems. Depending on the scientific and engineering questions that one desires to answer, various models have been employed to simulate polymeric systems at various spatiotemporal scales. For example, if one were to investigate the diffusion of nanoparticles within polymer thin films near a glass transition temperature, a coarse-grained model (that ignores the atomistic details of polymers but still captures the essential structure of polymers at large length scales) would be a proper model for molecular simulations. In this talk, I will briefly discuss the coarse-grained model for polymeric systems and illustrate how the coarse-grained model was used successfully to study important topics in polymeric systems. And as two simple examples, I will also talk about recent results from my research group: (1) the electrical conductivity and glass transition of polymer microfibers made of polymers and nanoparticles and (2) the fractional viscosity dependence of the loop formation kinetics in glass-forming liquids.

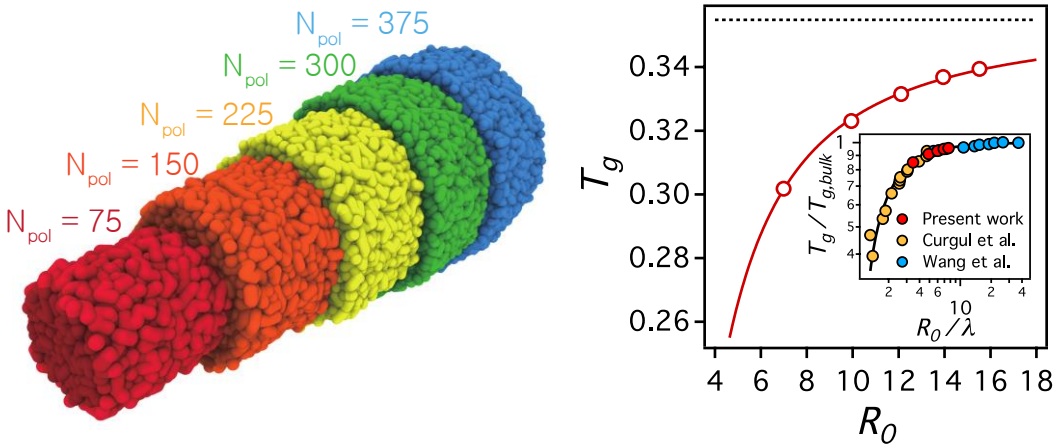

Fig. 1 Simulation Snapshot of polymer microfibers of various radii (left) and the glass transition temperature (Tg) as a function of the microfiber radius (R_0) (right). Inset is the relative value of Tg from various references.

References

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Quantifying Anomalous Transport in Living Cells: From Subdiffusion to Superdiffusion

Jae-Hyung Jeon*

Department of Physics, Pohang University of Science and Technology, Pohang, Korea

E-mail: jeonjh@postech.ac.kr

Biological cells are a sack of living matters of various sizes and species comprised of, e.g., the proteins, biopolymers, and organelles. It is known that the cells are supercrowded with these intracellular complexes beyond our naïve speculation, at a volume occupancy up to ~40% of the cell volume. For maintaining the living process various intracellular transport occurs in the cell. Experimental studies based on the state-of-the-art single particle tracking tools have shown that in such crowded and viscoelastic environments the particle movement usually disobeys the Einstein's simple law of Brownian diffusion, instead carrying out anomalous transport. Over the last decade the subdiffusion of various intracellular particles has been extensively studied on both experimental and theoretical sides [1,2]. Currently, a challenging task is to understand the motor-driven superdiffusive transport in the supercrowded living environments. In this talk, I overview the recent academic efforts for quantifying the intracellular transport in terms of the stochasticity and fluctuations shown in single-particle trajectory. It is shown that due to the activeness and the molecular crowding in living cells a variety of stochastically distinguished passive and active intracellular transports arise. It is demonstrated that the information on the stochastic characters and the ergodicity of the molecular motion is a fingerprint of identifying the physical origins of the anomalous transport as well as the clue for establishing a corresponding dynamic model. A number of popular anomalous diffusion models are also introduced.

References

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Scaling Law for Irreducible Entropy Production in Critical Systems

Junghyo Jo *

Asia Pacific Center for Theoretical Physics, Pohang 37673, Korea

E-mail: jojunghyo@apctp.org

Jarzynski derived a celebrated equality formulation for non-equilibrium processes. The Jarzynski equality, however, is deviated in absolute irreversible processes, and it is practically difficult to verify with finite sampling. We noticed that these two issues are naturally embedded in a quenching process across the critical point of second-order phase transitions. We considered the Ising model as a prototypical example for spontaneous symmetry breaking, and examined a quenching process from ordered to disordered spin states by controlling the ferromagnetic coupling constant. We then found that the entropy production during the quenching process followed a scaling law inherited from the critical scaling laws of second-order phase transitions. Our findings may provide an application of the Jarzynski equality to study the dynamical properties of phase transitions.

References

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Chemical Fluctuation Theorem for Stochastic Gene Expression

Ji-Hyun Kim

Creative Research Initiative Center for Chemical Dynamics in Living Cells, National Research Foundation of Korea-Chung-Ang University, Seoul 06974, Korea

Gene expression is a biologically pivotal process composed of a number of chemical reactions. The stochastic nature of gene expression outcome is varied depending on what target system is and which part of the system is essentially controlled. In order to understand the phenomena within a unified framework, we here present the chemical fluctuation theorem (CFT) relating the gene expression variability over single cells with the underlying chemical dynamics. In conjunction with a new mathematical approach for the transcription rate, which is coupled with intracellular environmental variables as well as a control variable, CFT enables to find a unified, quantitative understanding of mRNA copy number variations observed for various experimental systems. From the analysis, we demonstrate that new information about the transcriptional dynamics and mechanism can be drawn from the mean mRNA level-dependence of the non-Poisson mRNA noise. This work throws new light on quantitative investigations into cellular control over biological functions on the basis of a rigorous mathematical description.

Abstract

(1 월 24 일 오후)

Translational and Rotational Decoupling Using Tracers of Locally Favorable Structures in Glass-Forming Liquids

Yoonjae Park and Bong June Sung*

Department of Chemistry, Sogang University, Seoul 121-742, Republic of Korea

E-mail: bjsung@sogang.ac.kr

Near the glass transition, it is widely known that when dynamic heterogeneity [1] appears, the translation and the rotation of molecules decouple because of the Stokes-Einstein or Debye-Stokes-Einstein relations. A recent study shows that local media structure and tracer shape determine the trend of translation and rotation decoupling at least in two-dimension [2]. However, because of the weak structural information in 3D glassformers, it is hard to detect the local structures. Here, we use the topological cluster classification [3] to detect the energy minimum clusters and perform molecular dynamics simulations of Wahnström binary Lennard-Jones colloids [4] with tracers of three different shapes, i.e., Icosahedron, FCC, and HCP, which are long-lived and short-lived locally favorable structures [5]. For Icosahedron-tracer which is a long-lived locally favorable structure, the translation-rotation decoupling occurs and the high fraction of neighboring particles which are topologically same suppresses more the rotation relative to the translation. For other tracers, the decoupling is not significant compared to the Icosahedron tracer. The difference in the dynamics depending on the shapes of tracers indicates that there should be the connection between local structures and the dynamic heterogeneity.

References

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How to Obtain Accurate Adiabatic Energy Gap of Transition Metal Complexes

Suhwan Song and Eunji Sim*

Department of Chemistry, Yonsei University, Seoul 03722, Korea

E-mail: esim@yonsei.ac.kr

In this work, we present calculations for spin-crossover compounds using a recently proposed density-corrected density functional theory (DC-DFT) method. Because controlling spin states in spin-crossover systems is extremely difficult in experiments, one needs to use computationally costly methods like coupled cluster and quantum Monte Carlo for the energy difference between high- and low-spin states. Despite its efficiency and reasonable accuracy, density functional theory (DFT) fails to predict the right spin state consistently and accurately. Here we show that DC-DFT, in the form of HF-DFT, gives right prediction in spin states with quantitative accuracy comparable to coupled cluster results with a fraction of their computation cost. We envision such improvement in spin-crossover systems can be expanded to obtain correct spin-densities and ultimately to determine magnetization.

Prediction of Chlorosulfolipid (Danicalipin A) Membrane Structure Using Combined Coarse-Grained and Atomistic Model Simulations

Junyeal Lee and Rakwoo Chang*

Department of Chemistry, Kwangwoon University, Seoul 01897, Korea

E-mail: rchang@kw.ac.kr

Chlorosulfolipids (CSLs) are the major components of flagellar membranes in sea algae.[1] Unlike typical biological lipids with a hydrophilic head group and hydrophobic hydrocarbon tails, CSLs contain hydrophilic sulfate groups in the hydrocarbon tail region, which has hindered the prediction of the CSL membrane structure ever since they were first discovered in 1960.[2,3,4] Hence, we performed combined coarse-grained (CG) and atomistic molecular dynamics (MD) simulations to obtain some insights into the CSL membrane structure. First, The CG model based on Martina force fields was used to predict the mesoscopic membrane structure of CSLs. It was found that the CSL lipids form a stable monolayer membrane structure, in which the hydrocarbon moieties are sandwiched by hydrophilic sulfate groups in both head and tail regions. Based on these results, we performed atomistic MD simulations of the corresponding atomistic model and obtained a stable CSL membrane structure, in which the CSL lipids adopt a bent structure. In addition, we calculated the membrane thickness, area per lipids, and order parameter to show the membrane integrity. These results provide the significant information to understand the CSL membrane structure.

References

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Study of Glassy Systems with both Static and Dynamic Interactions in the Trajectory Space

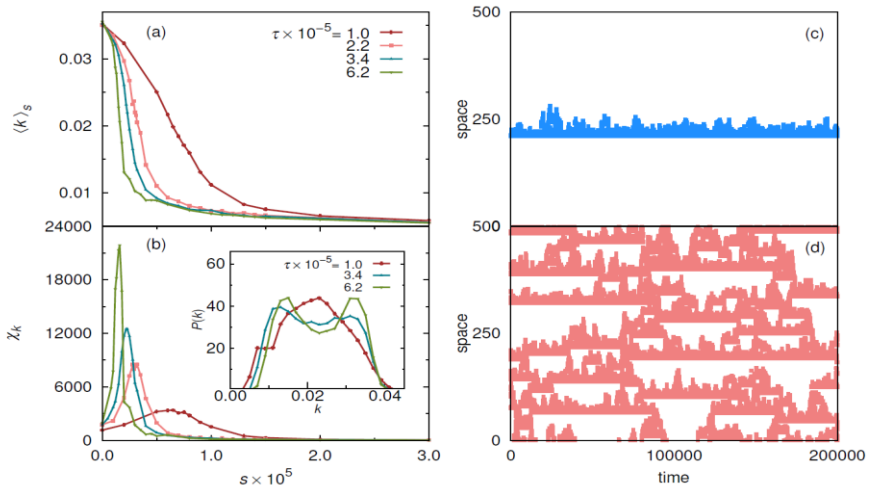
Chanwoo Noh, YounJoon Jung*

Department of Chemistry, Seoul National University, Seoul 08826, Korea

E-mail: eric8617@snu.ac.kr

yjjung@snu.ac.kr

Observing dynamical phase transition in s ensemble has been widely used to understand abnormal dynamic behaviors of supercooled liquids such as dynamic heterogeneity. [1,2] In this study, we provide the dynamical phase transition of an attractive East model. [3] Due to the kinetic constraint imposed in the model, active and inactive phases coexist at the critical point s^*. Analyzing the trajectories, it is shown that two phases are distinguished only by the number of mobile domains, not by the local structure of mobile domain. Moreover, the fact that proximity of s^* to zero is regarded as large dynamic fluctuation between two phases in equilibrium leads to the large dynamic heterogeneity for the strong attractive system.



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Chemical Fluctuation and Reaction Dynamics of Single Enzymes at Mesoscopic Concentrations

In-Chun Jeong,[1-3] Sanggeun Song,[1-3] Daehyun Kim,[1-3] Seong Jun Park,[1-3] Ji-Hyun Kim[1] and Jaeyoung Sung[1-3*]

[1]*Creative Research Initiative Center for Chemical Dynamics in Living Cells, Chung-Ang University, Seoul 06974, Korea.*

[2]*Department of Chemistry, Chung-Ang University, Seoul 06974, Korea.*

[3]*National Institute of Innovative Functional Imaging, Chung-Ang University, Seoul 06974, Korea.*

E-mail: jaeyoung@cau.ac.kr

We quantitatively investigate how the enzymatic turnover time distribution of enzyme systems depends on the number of enzymes and the microscopic reaction dynamics of enzyme-substrate complex. Assuming that the enzyme-substrate association reaction is the pseudo-first order reaction, we obtain simple and general equations for the enzymatic turnover time distribution and its first two moments. The obtained results could provide an unprecedented quantitative explanation of the experimental data for the dependence of the mean and variance of the enzymatic turnover times on the substrate concentration. By analyzing the distribution of enzymatic turnover times, we find that the lifetime distribution of the enzyme-substrate complex can be well approximated by a gamma distribution. We also examine the enzyme kinetics at physiologically relevant mesoscopic concentration of enzymes. For the enzyme system in the steady-state, which is relevant in most experimental situations, the MM equation is exact for the mean enzyme turnover rate at any concentration of enzymes, in spite of criticism against its validity at mesoscopic concentration of enzymes [1, 5].

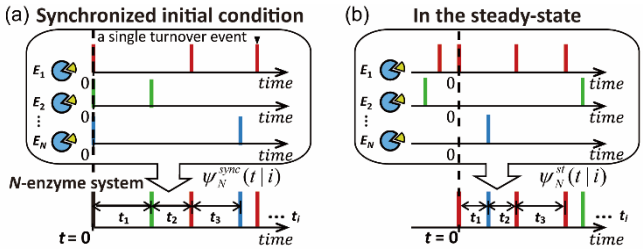

Fig. 1. A system of *N* enzymes (a) under the synchronized initial condition (b) in the steady state

References

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Abstract

(Poster)

Simulation Study of Shear Eexfoliation of Coarse-grained Graphene Model in a Liquid State

Inhyuk Jang and Bong June Sung*

Department of Chemistry, Sogang University, Seoul, 121-742, Korea

E-mail: bjsung@sogang.ac.kr

The dispersion exfoliation of graphene has been one of the most important topics. But it is difficult to produce a few-layered or a monomer graphene of high quality in a large quantity, because there is a strong Van der Waals interaction between stacked graphene layers inside graphite. There have been many conventional methods to exfoliate graphene, but most of them are not sufficiently effective. Contrast to the past conventional methods, shear exfoliation, however, based on the physical exfoliation method, is highlighted because of its high efficiency of producing a few-layered and defect-free graphene in a large quantity without using any harmful oxidants. We perform non-equilibrium molecular dynamics simulations to understand how does the shear force accelerate the graphene exfoliation. We construct the system with two parallel walls and put solvent particles and two graphene-like plates stuck strongly to each other. In order to mimic a shear experiment, we apply force to the upper wall and let the upper wall slide to the x-direction, which is parallel to the solvent flow. If the shear force were strong enough to overcome the attractive interaction between graphene plates, they would be separated. In this case, direct stochastic analysis of actual work applied on the plate is useful. So, by using the methods mentioned above, we investigate at a molecular level how two graphene-like plates get exfoliated.

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Identifying Molecular Conformation of C_3H_6S (thietane) by Theoretical Analysis of VUV/MATI Spectrum: 1 Dimensional Quantum-calculation

Chung Bin Park[1†], Yu Ran Lee[2†], Jiye Hwang[1†], Chan Ho Kwon[*2], Hong Lae Kim[*2] and Bong June Sung[*1]

[1]*Department of Chemistry, Sogang University, Seoul 121-742, Korea*, [2]*Department of Chemistry, Kangwon National University, Chuncheon 200-742, Korea*

E-mail: chkwon@kangwon.ac.kr, hlkim@kangwon.ac.kr and bjsung@sogang.ac.kr

Small heterocyclic molecules are important in chemical and biological field since they play a role as a reactant in many reactions and compose other complex compounds in nature. Their activities strongly depend on their molecular conformation [1]. In this respect, identifying the conformation of such molecules through a vibrational spectrum is important work. However, measuring and understanding the vibrational spectrum of heterocyclic molecules with a ring-puckering mode should be a challenging task. Due to a symmetry in this mode, the degenerate vibrational states appear near the minimum of potential energy surface (PES). On the other hand, near the top of the potential energy barrier, the degenerate states should be splitted with a small energy difference. In experiments, it is hard to observe such a small energy splitting. And even in theory, one should consider the symmetry of the PES to predict (or reproduce) the vibrational spectrum. Therefore, we develop a 1D quantum calculation method that considers the ring-puckering mode and its symmetry. We use trigonometric functions for basis sets and choose a puckering angle as a reaction coordinate. We successfully reproduce VUV/MATI spectrum (Kangwon National University. Chan Ho Kwon prof.) of thietane (C_3H_6S) with ring-puckering mode. We can assign each peak in the spectrum and calculate Franck-Condon factors and a Boltzmann factor to estimate the intensity of each vibrational transition. As a results, we find that the value of interconversion potential barrier and puckering anlge of the thietane cation ($48cm^{-1}$, 18.2°) are much smaller than those of the thietane neutral ($274cm^{-1}$, 26°) [2], where we could suggest that the conformation of the cation should be more planar than the neutral.

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Disorderly Disordered Disorder

TaeHwan Oh and Eunji Sim*

Department of Chemistry, Yonsei University, Seoul 03722, Korea

E-mail: esim@yonsei.ac.kr

We investigated the energy disorder in semiconductor nanocrystal (NC) systems. The energy disorder in nanocrystals is recognized as one of the key issues in controlling the carrier mobility in nanocrystals. For potential applications of granular electronic materials in electronic and optoelectronic devices, understanding the properties of semiconductor NCs has drawn much attention. However, the characteristics of NCs is largely affected by the polydispersity of NCs and, thus, it is important to explore the role of the energy disorder caused by the size disorder. We evaluate the energy disorder by employing the lognormal size distribution model and discuss the influence of the polydispersity on the carrier mobility of NC systems.

Spontaneous Transformation from Defected Nanosheets to Helical Structures

Sanghee Yoon and Eunji Sim*

Department of Chemistry, Yonsei University, Seoul 03722, Korea

E-mail: esim@yonsei.ac.kr

Soft helical nanostructures based on organic moieties can be obtained by self-assembly. Utilizing dissipative particle dynamics simulations with coarse-grained models, we program two-dimensional layer nanosheets with defects to self-roll into hollow helices or helix-like nanostructures. We show that the helical secondary structure can be controlled by defect patterns and densities. The sheet consists of lyophobic beads and simulation box was filled with theta solvent. Therefore, defected side causes anisotropy to the sheet self-transformation into a helix or a helix-like structure spontaneously. Self-rolled structure's radius and pitch are controlled by varying the defect width and the defect density.

Reaction between Molybdenum and Hydrogen Sulfide in Gas Phase

Seungsoo Nam and Eunji Sim*

Department of Chemistry, Yonsei University, Seoul 03722, Korea

E-mail: esim@yonsei.ac.kr

Transition metal dichalcogenides, especially MoS_2, is now attracting attention as a two-dimensional material with considerable band gap and reasonably high carrier mobility. The most widely used method for synthesizing MoS_2 is chemical vapor deposition. Although numerous techniques for the chemical vapor deposition of MoS_2 have been reported, there has been no report on the molecular-level reaction mechanism present in the chemical vapor deposition method. Here, using density functional theory, we have studied the early stages of MoS_2 formation. By calculating the stability and energy for various intermediates in the form of MoS_xH_y formed by the reaction of Mo and H_2S, we found a plausible gas phase reaction pathway that leads to solid MoS_2 formation.

Optoelectronic Properties of CdSe Nanocrystal Solids

Hyojin Kim and Eunji Sim*

Department of Chemistry, Yonsei University, Seoul 03722, Korea

*E-mail: esim@yonsei.ac.kr

In this presentation, we focus on the relationship between white light emission of CdSe nanoparticles and composition/coverage of ligands. In experiments, some ligands including trioctylphosphine oxide(TOPO), phosphonic acid, and amine have been reported to quench the broad trap state emission, whereas thiols raise the intensity of the trap state emission. This observation suggests that the regulation of white light emission is possible by means of ligand exchange, which certainly has been realized in experiments. However, fundamental understanding for the relationship between the ligand properties and the quenching/enhancement of the trap state emission has not been clarified yet. We employ density functional theory to investigate the role of ligands on the electronic structures of CdSe nanoparticles in presence or absence of various ligands. We show that the band gap structure, hence, the white light emission can be controlled by manipulating ligands not only by their distinctive chemical properties but also by the composition and the coverage of ligands.

Working Mechanism of Polyelectrolyte Diodes: Grand Canonical Monte Carlo Simulation Studies

Donghyuk Lee and Rakwoo Chang*

Department of Chemistry, Kwangwoon University, Seoul 01897, Korea

*E-mail: rchang@kw.ac.kr

In this study, we have performed Grand Canonical Monte Carlo (GCMC) simulations of primitive polymer models to understand the rectification mechanism of polyelectrolyte diode. Polyelectrolyte diodes, composed of oppositely charged double layer polyelectrolyte membranes and ions, have been a subject of active research because of their applications in lap on a chip and the new type of iontronic devices, and neural transmission[1]. Polyelectrolyte gels are modeled as charged melts of freely jointed hard chains and small ions as charged hard spheres. Two equilibrated oppositely charged polyelectrolyte gels are combined to form a polyelectrolyte diode. Grand Canonical Monte Carlo simulations of salt ion pairs are then performed to the polyelectrolyte diode system in the presence of electric field with various strengths. We examine the effects of applied voltage and gel concentration on the current flow. We observe rectification effects such that when negative voltage is applied (forward state), small ions start moving across the gel junction to induce electric current flow. On the other hand, when positive voltage is applied (reverse state), current flow diminishes significantly[2]. We also optimize gel concentration for maximum current flow and calculate electrostatic properties of semiconductor devices. The simulation results are in good agreements with previous experiments and provide some insights into the working mechanism of polyelectrolyte diode systems.

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Investigation of the Interaction between CEP55 and TEX14 Using Metadynamics Simulation

Yunju Cho and Rakwoo Chang*

Department of Chemistry, Kwangwoon University, Seoul 01897, Korea

E-mail: rchang@kw.ac.kr

Cytokinesis is the process in which the cytoplasm divides into two daughter cell after nuclear division in the cell division. In somatic cell, cytokinesis requires ALIX (or TSG101) and the midbody protein centrosomal protein 55 kDa (CEP55) to activate cell abscission. In germ cell, in contrast, CEP55 forms intercellular bridges with testis-expressed gene 14 (TEX14), by which the cell abscission is blocked.[1,2,3] These intercellular bridges also play important roles in synchronization of germ cells, especially in spermatogenesis, by passage of organelles and molecules between germ cells. If TEX14 is deleted intentionally, intercellular bridges are disrupted and it causes sterility.[1,2] Also, these abilities of TEX14 may provide information on inactivation of the abscission to suppress the proliferation of cancer cell. However, the detailed information about how TEX14 interacts with CEP55 to prevent cell abscission is still insufficient. Hence, to obtain more specific details about interaction between CEP55 and TEX14, which is not easy to identify in experiments, we performed metadynamics simulations using atomistic models of CEP55 and TEX14. Our results show that Tyr801 residue of TEX14 forms a strong hydrogen bond with Glu192 residue of CEP55, which is consistent with previous experimental studies.[1,3] The binding Gibbs free energy surface calculated by the metadynamics simulation is also in good agreements with experimental data.[1] In the future, we plan to study other peptides containing $GPPx_3Y$ motifs of TEX14 as a candidate for the suppressor of cancer cell proliferation.

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Thermoresponsive Collapse-swelling Transition of a Single Poly(N-isopropylacrylamide) Chain in Water

Yunwon Kang and Jun Soo Kim*

Department of Chemistry and nanoscience, Ewha Womans University, Seoul 03760, Korea

E-mail: jkim@ewha.ac.kr

Poly(N-isopropylacrylamide) (PNIPAM) is well known thermoresponsive polymer. It shows lower critical solution temperature (LCST) around 32 °C in aqueous solution. At temperatures below the LCST, PNIPAM is soluble in water with swollen polymer conformations, whereas it becomes collapsed at temperatures above the LCST.

We present molecular dynamics (MD) simulations of a single 30-mer PNIPAM chain in explicit water at temperatures between 270 and 320K near the LCST. The force-fields of OPLS-AA and TIP4P/2005 are used for a PNIPAM chain and water molecules, respectively. Three independent simulations with durations of 1 μs are performed at each temperature starting with three different conformations: extended, loosely collapsed, and tightly collapsed states. The simulations trajectories exhibit reversible conformational transitions between swollen and collapsed-chain conformations, with the overall transition occurring at different temperatures depending on the initial conformation.

The simulations trajectories are analyzed in terms of the radius of gyration, intrachain distances, hydrophobic contacts, and chain-water and intrachain hydrogen bonding. In particular, the formation of stable intrachain hydrogen bonds is a signature of the tightly collapsed-chain conformations that persist, once formed, for the entire simulation duration.

Directional Rolling of Nanoparticles on Long DNA Molecules along a Gradient of DNA Flexibility

Suehyun Park, Heesun Joo and Jun Soo Kim*

Department of Chemistry and nanoscience, Ewha Womans University, Seoul 03760, Korea

E-mail: jkim@ewha.ac.kr

Directing the motion of molecules/colloids along any specific direction can be of a great interest in many applications of chemistry, physics, and biological sciences, where regulated positioning or transportation of materials is highly desired. Using Brownian dynamics simulations of coarse-grained models of lengthy DNA molecules and positively charged nanoparticles, we observe that the motion of single nanoparticles bound and wrapped on a lengthy DNA molecule can be directed along a gradient of DNA local flexibility. The flexibility gradient is constructed along a 0.8 kilobase-par DNA molecule such that local persistence length decreases gradually from 50 nm to 40 nm, mimicking gradual decrease of a ratio of AT to CG base pairs in local DNA regions. Nanoparticles roll over a length DNA molecule from less flexible regions towards more flexible ones due to the decreasing energetic cost of DNA bending. This work suggests that the variation in DNA local flexibility can be utilized in constructing and manipulating supramolecular assemblies of DNA molecules jointed or functionally decorated by specific positioning of nanoparticles

The Collapse of Polymer Brush in Good Solvents Mixture

Gyehyun Park and YounJoon Jung*

Department of Chemistry, Seoul National University, Seoul 151-747, Korea

E-mail: kyehyun3950@snu.ac.kr, yjjung@snu.ac.kr

Water and methanol are good solvents for poly(N-isopropylacrylamide) grafted brush, but this brush collapses in the water-methanol mixture. This abnormal phenomenon, called cononsolvency, has been drawing attention due to its practical application for stimuli-responsive polymer brush. In this work, the physical origin of the cononsolvency in polymer brush system is presented by using molecular dynamics simulation. The macromolecules are modeled as coarse grained bead springs solvated in the Lennard-Jones particles. Varying the solvents composition, we obtain the average thickness of polymer brush, which is in agreement with experiment. The density profile of each solvents shows that the cononsolvecy is caused by the competitive absorption of solvents. This preferential attraction between the polymer and solvent also induce the non monotonic behavior of dynamical property such as viscosity as well as structural property.

The Depletion Attraction on the Simple Ring DNA Model

Inrok Oh[†], Saehyun Choi[‡], YounJoon Jung[†*] , Jun Soo Kim[‡*]

†Department of Chemistry, Seoul National University, Seoul 08826, Korea

‡Department of Chemistry and Nanoscience, Ewha Womans University, Seoul 03760, Korea

†E-mail: yjjung@snu.ac.kr

‡E-mail: jkim@ewha.ac.kr

The crowding effect is the induced attraction between macromolecules in existence of crowding agents such as proteins and nucleic acids. To investigate the microscopic behavior of DNA in the crowded condition, densely and sparsely collapsed DNA models are generated using heterochromatin and euchromatin fiber densities respectively. The depletion potential induced by the crowding agents is successfully converted to the attraction with the heterochromatin model. However, the depletion potential is vanished with the euchromatin model in the same crowded condition due to the fluffy surfaces of euchromatin model. The ring DNA models that comprise the thirty members of heterochromatin or euchromatin model are introduced to investigate the influences of depletion potential on the ring compactness and interaction between ring members. The depletion attraction between ring members does not influence the compactness of ring DNA due to the its narrow acting range. However, the depletion attraction prolongs the interaction time between two DNA that have large contour length when they approach. In other words, the depletion attraction supports to make and maintain rosette like structure of DNA.

Phase-separating Behavior in the Fluctuating Observation Time Eensemble

Hyuntae Lim and YounJoon Jung *

Department of Chemistry, Seoul National University, Seoul 151-747, Korea

E-mail: ht0620@gmail.com, *yjjung@snu.ac.kr*

We simulate simple phase-separating lattice gas model with short-ranged nearest neighbor interactions to illustrate kinetic trapping in the self-assemble process. It is widely known that kinetic trapping doing key role in self-assembling systems. Irreversible behavior in short time scale makes the system difficult to reach ordered equilibrium structure. We use the transition path sampling and the fluctuating observation time ensemble (aka. x-ensemble) method in stochastic Markov process to control dynamics, avoid the trap, and obtain efficiently assembled configurations. And we investigate correspondence dynamical properties of both equilibrium and non-equilibrium system.

Effects of Alkyl Chain Length on Interfacial Structure and Differential Capacitance in Graphene Supercapacitors : A Molecular Dynamics Simulation Study

Sungsik Jo,[†] Sang-Won Park,[†] Youngseon Shim,[*,†,1] and YounJoon Jung[*,†]

[†]*Department of Chemistry, Seoul National University, Seoul, 151-747, Korea,*

[*]E-mail:sung8802@snu.ac.kr, cocoon-1@snu.ac.kr, ddalgi1231@gmail.com, yjjung@snu.ac.kr

Supercapacitors with graphene electrodes are studied via molecular dynamics simulation. As an electrolyte, we consider three different room-temperature ionic liquids (RTILs), each of which is made up of the same anion BF_4^-, and different cations, 1-ethyl-3-methylimidazolium ($[emim]^+$), 1-butyl-3-methylimidazolium ($[bmim]^+$), and 1-hexyl-3-methylimidazolium ($[hmim]^+$), respectively. We investigate how the alkyl chain length of the cation affects their interfacial structure and electrical properties for electrical double layer capacitors (EDLCs). As a whole, cations and anions make layering structures between two parallel electrodes. Cations in the nearest layer orient predominantly in parallel to the electrode. Imidazolium rings of cations form π-stacking with graphene, then the alkyl chains of cations align parallel to the electrode. Differential capacitances in three RTILs are found to decrease with an increase of the magnitude of electrode potentials. The ion size and orientation affect both structure and capacitance behavior. We find that the parallel orientations of cations become stronger with an increase of the alkyl chain length for the considered RTILs. The differential capacitance tends to decrease with raising the alkyl chain length over a wide range of the electrode potential. This is ascribed to a steric effect caused by larger cation size. It is also found that anodic capacitance is higher than cathodic one due to a higher screening efficiency by small anions, and an asymmetry in the peak of capacitance biased to the cathodic side becomes weaker as the alkyl chain length increases. By comparing electrode charge with a change in ion numbers near the electrodes, we find that capacitive behavior of our systems is mainly governed by the interfacial layer of the electrolyte.

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[1] Present Address

Samsung Advanced Institute of Technology, Yongin-si, Gyeonggi-do, South Korea

Dynamical Phase Transition of the One-dimensional Ising Model

Jaehak Lee and YounJoon Jung*

Department of Chemistry, Seoul National University, Seoul 08826, Korea
E-mail: dlwogkr1228@snu.ac.kr, yjjung@snu.ac.kr

In this study, we present a dynamical phase transition of the one-dimensional Ising model through the dynamical trajectory ensemble. The trajectory ensemble, also known as the *s* ensemble, is a methodology for sampling non-equilibrium trajectories by introducing a biasing field, *s*, which is conjugated to a dynamical variable of trajectory. It is known that there is no phase transition in the one-dimensional Ising model in the thermodynamic equilibrium state when magnetic field is zero. However, through the *s* ensemble, we find that there is a dynamical phase transition in the one-dimensional Ising model. The dynamical phase transition in one-dimensional Ising model is seems to relate to the equilibrium phase transition of the two-dimensional Ising model because of the same universality. Finite size scaling law, which is widely used in statistical mechanics, can be applied to the dynamical phase transition as well.

Power Spectrum of the Iintracellular Chemical Noise: A Useful Probe of Non-classical Reaction Dynamics in Live Cells

Gil-Suk Yang[1-2], Sanggeun Song[1-3], Ji-Hyun Kim[1], and Jaeyoung Sung[1-3]

1 National CRI-Center for Chemical Dynamics in Living Cells, Chung-Ang University, Seoul 06974, Korea.

2 Department of Chemistry, Chung-Ang University, Seoul 06974, Korea.

3 National Institute of Innovative Functional Imaging, Chung-Ang University, Seoul 06974, Korea.

In living cells, the power spectrum of creation rate fluctuation contains rich information about the reaction mechanism and dynamics of the product creation process. However, it is very difficult to directly measure the power spectrum of creation rate fluctuation. Here, we present the general formulation of the power spectrum of product number fluctuation, which can be used to extract the power spectrum of the product creation rate fluctuation. As long as the decay of the product obeys the first-order kinetics, the result is exact regardless of stochastic property of the product creation rate fluctuation, so it is particularly useful in investigating the chemical dynamics of vibrant reaction processes and its consequence in living cells. Application of our result is made to analyze time traces of protein copy number from a stochastic gene expression model of mouse embryonic stem cell. It is shown that the information about the distribution of silent transcription intervals, which is difficult to be obtained by using contemporary experimental techniques, can be extracted from the power spectrum of the protein level fluctuation.