Role of bond orientational order in the homogeneous crystallization from supercooled liquids

John Russo and Hajime Tanaka

Institute of Industrial Science, University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo

During crystallization the liquid loses both its translational and orientational symmetry, but how the symmetry breaking occurs microscopically is still a matter of debate. Classical approaches (like Classical Nucleation Theory) assume that the crystallization process is primarily controlled by positional order, with the liquid regarded as a spatially uniform background where nucleation can occur at any location with equal probability. Recent studies have instead shown that the process is far from classical. In particular the crystallization pathway has been described by a two-step process, in which the first step involves the formation of dense amorphous precursors, and the second step consists in the emergence of crystalline order from these precursors. On the other hand, recent simulation works have pointed out the importance of bond orientational order [1].

In the present contribution we will examine in detail the crystallization process for different supercooled liquid models (hard spheres, gaussian core model, mW water), showing that the actual microscopic pathway is different from what previously thought. The transition is driven by fluctuations of bond orientational order [2,3]. This leads to a prestructuring of the nuclei prior to densification, in analogy with early observations of crystallization in molecular systems. Following the development of bond orientational order, we will show that the selection of the polymorph to be nucleated starts early in the metastable liquid, and it is not simply related to the bulk properties of the stable phases (as implied, for example, in Ostwald's step rule of nucleation) [2,3]. With a two-order parameter description of the metastable liquid, we will show that the formation of metastable crystal nuclei is limited at low densities by disordered fluid configurations, and at high densities by dense aggregates with five-fold symmetry [3]. This provides a justification of Frank's hypothesis on the role of icosahedral clusters in disfavoring the crystallization process. This observation suggests a deep link between crystallization and vitrification.

Multiple spatiotemporal structures of dynamic heterogeneities in glass-forming liquids: Probing multi-point and multi-time correlations

Kang Kim\textsuperscript{A}, Shinji Saito\textsuperscript{A}, Kunimasa Miyazaki\textsuperscript{B}, Giulio Biroli\textsuperscript{C}, and David Reichman\textsuperscript{D}

\textsuperscript{A)Institute for Molecular Science, Okazaki, Japan}
\textsuperscript{B)Institute of Physics, University of Tsukuba, Japan}
\textsuperscript{C)Institut Physique Theorique, CEA Saclay, France}
\textsuperscript{D)Department of Chemistry, Columbia University, USA}

The notion of "dynamic heterogeneity" in glass-forming liquids has attracted much attention and has been considered central to understanding the slow dynamics of glasses. It is now needed to characterize and quantify the length and time scales to determine the physical role of dynamic heterogeneities in the underlying mechanism of the glassy slow dynamics.

(1) Recently, three-point correlation functions are introduced to characterize growing length scales associated with spatially heterogeneous dynamics in glass-forming liquids based on the mode-coupling theory. This theoretical treatment is referred to as the inhomogeneous mode-coupling theory (IMCT) \cite{1}. In our study, according to the procedure of the IMCT, we utilize a non-equilibrium molecular dynamics simulation, where the system is perturbed by the external potential coupled with the spontaneous density field. Here, it is demonstrated that the length scale is quantified from the wave number dependence of the three-point correlation function. We also determine the dynamic length scales from the four-point correlation functions, which have been already well studied. Various scaling properties regarding these length scales are examined in the comparison with the theoretical predictions of IMCT \cite{2}.

(2) We report an extensive and systematic investigation of the multi-time correlation functions to reveal the temporal structures of dynamic heterogeneities in glass-forming liquids \cite{3}. Molecular dynamics simulations are carried out for the supercooled states of various prototype models of glass-forming liquids. Our results indicate that the lifetime of the dynamical heterogeneities becomes much longer than the $\alpha$-relaxation time determined from a two-point correlation function in fragile glasses. The decoupling between the two time scales is remarkable, particularly in supercooled states, and the time scales differ by more than an order of magnitude in a more fragile glass. In contrast, the lifetime is shorter than the $\alpha$-relaxation time in tetrahedral network-forming strong glass, even at lower temperatures \cite{4}.

\cite{2} K. Kim, \textit{et al}., in preparation.
\cite{4} K. Kim and S. Saito, submitted to J. Chem. Phys. as a part of Special Topic in Glass Transition.
Molecular dynamics simulations of fullerenes: from nanofluidics in carbon nanotubes to fragmentation of buckyballs

T. A. Beu
University Babes-Bolyai, Faculty of Physics, I Mihail Kogalniceanu, 400084 Cluj-Napoca, Romania

A. Extensive MD simulations of the ionic transport in aqueous solutions through carbon nanotubes, based on the longest data collection times reported in the literature (on the microsecond scale), are presented. Distinctive modeling features worth mentioning are: quaternion-based rigid-body dynamics for the water molecules; up-to-date polarizable site-site interaction models for the water molecules and novel charge-on-spring type polarizable models for the solute ions; state-of-the-art mesh-based FFT-accelerated Ewald sum techniques to handle the long-range Coulomb interactions in conjunction with periodic boundary conditions; polarized nanotube charges calculated by novel Monte Carlo methodology. The effects of the nanotube radius, solute concentration, and applied electric fields on the solution structuring are explained in terms of spatial density distributions, pair distribution functions, and detailed electrostatics. The structural features are consistent with experimental evidence and general theoretical nanofluidics results (for example, logarithmic dependence of the Donnan-type voltages on the maximum ion concentration). The transport properties are characterized by mobilities, currents, and pairing of the solute ions and corroborate, equally, experimental data and general nanofluidics results (for example, the solute concentration dependence of the nanochannel conductance and the current-voltage curve). Discontinuities in the partial ionic currents are explained on the basis of a recent theoretical model of quantized ionic conductance in nanopores. Correlations between the structural and dynamic properties are established, linking causally the highly structured spatial density profiles, the ion pairing phenomenon, and the ionic currents. The control of the ionic transport by superficial pore charges is investigated and the fine-tuning role of the induced dipole interactions and the polarization of the nanotube charge is analyzed.

B. The radiation induced fragmentation of the fullerenes C36, C60, C70, and C96 is investigated by tight-binding molecular dynamics simulations. The calculations are based on a validated non-orthogonal tight-binding parametrization scheme and account explicitly for the non-adiabatic excitation of the fullerenes and the charge-transfer processes undergone by the resulted fragments. The simulated fragment size and fragment charge distributions, averaged over large ensembles of trajectories corresponding to total ionization states up to +20e and excitation energies up to 300 eV, have been used to characterize the fragmentation statistics in terms of several derived quantities (fragmentation probability, number of fragments, fragment size, number of bonds). Clearly delimited phase transition regions have been identified in the excitation energy dependences of the fragmentation probability for all fullerene species,
which separate fragmentationless regions from certain-fragmentation plateaus. The critical points appear to depend to a fair approximation on the squares of the total ionization charge and linearly on the fullerene size. Moreover, the charge averaged critical excitation energies estimated from the parabolic models have been found to depend linearly on the fullerene size. Comparisons with recent experiments evidence fair agreement of the critical excitation energies.

Effects of homogeneous thermostats on the computation of nonlinear rheological properties

Peter Daivis A, Benjamin Dalton A, and Tetsuya Morishita B

A) RMIT University Melbourne Australia
B) AIST Tsukuba Japan

Thermostats for homogeneous non-equilibrium molecular dynamics simulations are usually designed to control the kinetic temperature, but it is now possible control any combination of many different types of temperature, including the configurational and kinetic temperatures and their directional components. It is well known that these temperatures can become unequal in homogeneously thermostatted shearing steady states. The microscopic expressions for these temperatures are all derived from equilibrium distribution functions, and it is pertinent to ask, what are the consequences of using these equilibrium microscopic expressions for temperature in thermostats for shearing non-equilibrium steady states? Here we show that the answer to this question depends on which properties are being investigated. We present numerical results showing that the value of the zero shear rate viscosity obtained by extrapolating results of non-equilibrium molecular dynamics simulations of shearing steady states is the same, regardless of the type of temperature that is controlled. It also agrees with the value obtained from the equilibrium stress autocorrelation function via the Green-Kubo relation. However, the values of the limiting zero shear rate first normal stress coefficient obtained from non-equilibrium molecular dynamics simulations of shearing steady states are strongly dependent on the choice of temperature being controlled, They also differ from the value of the first normal stress coefficient that is calculated from the equilibrium stress autocorrelation function. We show that even when all of the directional components of the kinetic and configurational temperatures are simultaneously controlled to the same value, the agreement with the result obtained from the equilibrium stress autocorrelation function is poor.
A molecular dynamics study of thermal conductivity for the Lennard-Jones system in the harmonic and anharmonic approximation

Hideo Kaburaki

Japan Atomic Energy Agency

There is an increasing interest in evaluating lattice thermal conductivity for developing thermoelectric materials with high figure of merit, and various simulation methods, such as the conventional anharmonic lattice dynamics method and the molecular dynamics method with the Green-Kubo formula, have been employed. The Green-Kubo method is formally exact, but the range of statistical uncertainty, which arises from molecular dynamics simulations, is not systematically checked due to the requirement of computational resources. On the other hand, the anharmonic lattice dynamics method based on the expansion of the crystal potential has been frequently employed to evaluate thermal conductivity, however, its theoretical framework is too complex to prove the validity of each process numerically.

Here, we adopt the molecular dynamics method coupled with the Green-Kubo formalism to evaluate thermal conductivity on the Lennard-Jones argon system. We evaluated the temperature dependence of thermal conductivity of solid argon with $N=864$ and the long range cutoff length of $4\sigma$ (unit of length), and found that the results were in good agreement with experiment [1]. A study on the effects of the system size and the statistical averaging, which appear sensitively in the heat flux autocorrelation function, is especially important to understand the dynamical properties of the system, although the integrated quantity of thermal conductivity is very close to experiment [2]. Here, the relation of the shift time and the number of ensembles in the statistical averaging process is found to derive the appropriate sampling method. The system size dependence on the correlation function shows that fluctuations converge on the system of 2048 particles. The correlation is found to consist of two processes, rapidly and slowing decaying (phonon) parts, and the power spectrum clearly shows the resonance peak between these processes in the lower temperature region. The validity of the expanded crystal potential of the harmonic and anharmonic (third and fourth order) approximation, frequently employed in the calculation of thermal conductivity for the phonon Boltzmann equation, is studied by the classical molecular dynamics method with the Green-Kubo formalism. The agreement with the LJ system is good in the lower temperature region. The results on the temperature dependence clearly show how this approximation fails in the higher temperature region.


The hard-disk model has exerted outstanding influence on computational physics and statistical mechanics. Decades ago, hard disks were the first system to be studied by Markov-chain Monte Carlo methods[1] and by molecular dynamics[2]. It was in hard disks, through numerical simulations[3], that a two-dimensional melting transition was first seen to occur even though such systems cannot develop long-range crystalline order. Analysis of the system was made difficult by the absence of adequate simulation methods.

In recent years, we have developed a number of powerful Monte Carlo algorithms for hard disks and related systems[3-6]. In particular, the event-chain Monte Carlo algorithm has allowed us to show that hard disks melt with a first-order transition from the liquid to the hexatic and a continuous transition from the hexatic to the solid[7]. Results obtained with this methods have now been checked independently. I will outline the computational ideas for serial and parallel computing, for which the hard-disk problem serves as a beautiful example and a most prominent benchmark.

Design rules for the self-assembly of a protein crystal

Thomas K. Haxton and Stephen Whitelam
Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

Prominent models of protein crystallization represent proteins as spheres and protein crystals as close-packed structures. They are motivated by two observations. First, phase diagrams for typical protein solutions and for spherical colloids with short range attractions are structurally similar: both contain a demixing transition between a vapor of solute (solute-poor solution) and a liquid of solute (solute-rich solution) that is metastable with respect to crystallization [1]. Second, both proteins and spherical colloids tend to crystallize when the second virial coefficient, an orientationally-averaged measure of solute-solute attraction, lies in a defined `crystallization slot' [2]. On the computer, such spherical models crystallize poorly above the binodal describing the demixing transition and show enhanced nucleation rates near or below it [1, 3]. Similar enhancement is indeed seen in some protein solutions [4], but other experiments show disparities with this picture. Proteins can crystallize readily above the binodal [5] and experience kinetically-impaired crystallization below it [6]. They can also lie in the crystallization slot and not crystallize [7].

Here, we argue that these disparities are expected on the grounds that proteins and spherical colloids form crystal structures of different nature [8]. Many protein crystals have open crystal structures, often with multiple protein monomers per unit cell, and are stabilized by anisotropic interactions. We have used theory and simulation to demonstrate that the design rules governing the self-assembly of one such crystal differ profoundly from those governing close-packed crystals. The second virial coefficient is not a predictor of efficient assembly, and liquid-vapor demixing generally suppresses crystallization. Instead, good assembly requires a thermodynamic driving force of about $k_BT$ and an optimization of interaction specificity. In experimental terms, our results suggest adjusting solution conditions in order to impose a defined supersaturation at the liquid-vapor binodal.

One plausible strategy for further enhancing assembly of crystals with complex unit cells is to promote the initial assembly of oligomeric building blocks followed by their subsequent crystallization. Surprisingly, we find that this strategy reduces the efficiency of crystallization in our model system. Tuning interactions to favor assembly of the intermediate building blocks leads to two types of kinetic trapping which we expect to be generic: the nonspecific aggregation of intermediate building blocks hampers growth of the target crystal, and rapid depletion of the pool of monomers can lead to partially formed intermediate complexes that cannot combine to form the target crystal.

Molecular dynamics studies of material dynamics: 
from petascale to exascale

Timothy C. Germann

Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM 87545 USA

Computational materials scientists have been among the earliest and heaviest users of leadership-class supercomputers. The codes and algorithms which have been developed span a wide range of physical scales, and have been useful not only for gaining scientific insight, but also as testbeds for exploring new approaches for tackling evolving challenges, including massive (nearly million-way) concurrency, an increased need for fault and power management, and data bottlenecks. As examples, I will describe our classical molecular dynamics simulations as early users on the LLNL BG/L and LANL Roadrunner platforms, including in situ analysis and visualization of trillion-atom simulations. Multiscale, or scale-bridging, techniques are attractive from both materials science and computational perspectives, particularly as we look ahead from the current petascale era towards the exascale platforms expected to be deployed by the end of this decade. In particular, the increasingly heterogeneous and hierarchical nature of computer architectures demands that algorithms, programming models, and tools must mirror these characteristics if they are to thrive in this environment. Given the increasing complexity of such high-performance computing ecosystems (architectures, software stack, and application codes), computational “co-design” is recognized to be critical as we move from current petascale to exascale supercomputers over the rest of this decade. The Exascale Co-design Center for Materials in Extreme Environments (ExMatEx) [1] is an effort to do this by initiating an early and extensive collaboration between computational materials scientists, computer scientists, and hardware manufacturers. Our goal is to develop the algorithms for modeling materials subjected to extreme mechanical and radiation environments, and the necessary programming models and runtime systems (middleware) to enable their execution; and also influence potential architecture design choices for future exascale systems.

Relaxation dynamics of jamming soft spheres

Takahiro Hatano

Earthquake Research Institute, the University of Tokyo

hatano@eri.u-tokyo.ac.jp

In general, thermal or athermal particulate systems at high density, the structural rearrangement is difficult due to the exclusion volume effect so that the structural relaxation time and the viscosity drastically increase. In particular, zero-temperature systems such as granular materials or emulsions acquire the elastic moduli above a certain density [1]. This rigidity transition, which is also referred to as the jamming transition, is accompanied by some power-law behaviors that are characteristic to critical phenomena [2], e.g., the growing correlation length in terms of spatially heterogeneous diffusion. Indeed, such dynamical heterogeneities are also observed in thermal systems such as supercooled liquids and dense colloids. This suggests the potential relation between the glass and jamming transitions, although still controversial.

Here we simulate a relaxation process of non-Brownian particles in a sheared viscous medium; the system is subject to the small shear strain and then undergoes relaxation. Cooperative motion of particles in structural relaxation is analyzed. In particular, we estimate the exponents with which the relaxation time and the correlation length diverge as the density approaches the jamming density from below [3]. Interestingly, the dynamic critical exponent is estimated as 4.6, which coincides that for a supercooled liquid [4]. It is also found that shear stress undergoes power-law decay at the jamming density, which is reminiscent of critical slowing down.

This study was supported by the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan, under its Observation and Research Program for Prediction of Earthquakes and Volcanic Eruptions.

Huge-Scale Molecular Dynamics Simulation of Cavitation Process

Hiroshi Watanabe A, Masaru Suzuki B, and Nobuyasu Ito C
A) The Institute for Solid State Physics, The University of Tokyo
B) Department of Applied Quantum Physics and Nuclear Engineering, Kyushu University
C) Department of Applied Physics, School of Engineering, The University of Tokyo

We have developed molecular dynamics codes for short-range interaction potential which adopts the both flat-MPI and MPI/OpenMP hybrid parallelization on the basis of a fully domain decomposition strategy. Benchmark simulations containing up to 38.4 billion Lennard-Jones particles were performed on PRIMEHPC FX10, consisting of 4800 SPARC64 IXfx 1.848 GHz processors, at Information Technology Center of the University of Tokyo, and achieved performance of 193 TFLOPS which is 17.0% execution efficiency. Cavitation processes were also simulated involving 1.45 billion particles on PRIMEHPC FX10 and 22.9 million particles on SGI Altix ICE 8400EX at the Institute of Solid State Physics of the University of Tokyo. Ostwald-like ripening was observed after multi-bubble nuclei. Our results demonstrate that direct simulations of multi-scale phenomena involving phase transitions from atomic scale become possible and the molecular dynamics method is one of the promising applications that can utilize peta-scale computers.

Figure 1: Snap shots of a cavitation process. The direction of time evolution is left to right. Multi-bubble nuclei and the Ostwald-like ripening are observed.

Figure 2: Late stages of the Ostwald-like ripening. Only one bubble has survived in the system.

Velocity fluctuations and behavior of diffusion at finite peclet number

Adnan Hamid\textsuperscript{A}, and Ryoichi Yamamoto \textsuperscript{A}

Department of Chemical Engineering Kyoto University, 615-8510, Kyoto, Japan

A direct numerical simulation (DNS) using smooth profile (SP) \cite{1} method has been performed to investigate the steady state sedimentation of monodispersed hard spherical particles in an incompressible fluid at finite Peclet number (Pe) under periodic boundary conditions. In contrast to non-Brownian regime, sedimentation at finite Pe number describes the relative effects of thermal fluctuations and hydrodynamic fluctuations \cite{2}. To differentiate between the effects of hydrodynamic and thermal fluctuations, we define the temporal velocity fluctuations auto correlation functions. We found that the relaxation time is different for the vertical and horizontal direction. This difference in time scales arises from the periodic boundary condition used. In the experimental study \cite{3} it was found that these correlation function relax of the form $C_\alpha(t) = \langle \Delta V_{\mu}^\alpha \rangle \exp(t/\tau_{\mu}^\alpha)$, where $\Delta V_{\mu}^\alpha$ and $\tau_{\mu}^\alpha$ denote the amplitude and the relaxation time of the hydrodynamic velocity fluctuations, respectively. Cunha et al. \cite{4} predicted the scaling relations as $\Delta V_{\mu}^\alpha / V_\alpha^\alpha = \sqrt{A_1^\alpha L \phi / a}$ and $\tau_{\mu}^\alpha / t_\alpha = A_2^\alpha \sqrt{L \phi / a}$ where $A_1^\alpha$ and $A_2^\alpha$ are the constants that can be found by exponential fit on the velocity autocorrelation function. We also found that ratio of vertical to horizontal hydrodynamic velocity fluctuations is 2.36, is in good agreement with the experiments. Diffusion refers to the fluctuating motion of the particles. To examine the anisotropic particle diffusion in sedimentation, we consider the total diffusion constant as the sum of thermal and hydrodynamic diffusion coefficient, which can be estimated by aforementioned scaling arguments as $D_{\mu}^\alpha \approx \left( \Delta V_{\mu}^\alpha \right)^2 \tau_{\mu}^\alpha = A_1^\alpha A_2^\alpha D_o Pe^{1/2} (L / a)^{3/2}$, whereas vertical diffusion having larger prefactors than horizontal diffusion. These scaling arguments indicate that the vertical and horizontal diffusion coefficients increase linearly with Pe. Our simulations show good agreement with the predictive equations. We also found that anisotropy in diffusion increased linearly with Pe, plateauing at a value of $\approx 25$, in good agreement with the predicted scaling argument. The anisotropy achieved is relatively higher than the one reported in the experimental study. This higher value is attributed to the cubic periodic box and periodic boundary conditions used.

\begin{thebibliography}{9}
\bibitem{2} Padding JT, Louis AA. Phys.Rev. E 2008; 77,011402
\bibitem{4} Cunha FR, Abade GC, Sousa AJ, Hinch EJ. J Fluids Eng. 2002; 124,957-968
\end{thebibliography}
Semiquantum Molecular Dynamics Simulation of Liquid Water
-Microscopic, Mesoscopic, and Macroscopic Dynamic Properties-

Kim Hyeon-Deuk, and Koji Ando

Department of Chemistry, Kyoto University, Kyoto, JAPAN, 606-8502

Many important chemical and biochemical reactions take place in liquid water, and many classical and empirical water models have been proposed to achieve better agreement with experimental results. Its rigorous quantum calculations are too complicated to be applied to a complex and large condensed system, so various semiquantum approaches such as centroid molecular dynamics (CMD) and ring polymer molecular dynamics (RPMD) have been developed and applied in recent years.

We have developed the new semiquantum water (SQW) molecular dynamics (MD) simulation method. [1] Here, the wave packet (WP) approach was for the first time applied to study condensed bulk water structure and dynamics. In order to account for nuclear quantum effects such as the zero point energy and WP delocalization, we described each hydrogen atom as a three-dimensional Gaussian WP basis function. Our SQW MD simulation requires only the additional equations of motion for the WP width and its momenta, and the computational cost is much cheaper than other semiquantum approaches. Nevertheless, our SWQ simulation successfully reproduced the major properties of CMD and RPMD; the quantized water is less structured, the diffusion coefficient is larger than is seen in classical simulations, and the IR spectrum of the OH stretching mode is red-shifted. Furthermore, we found a new peak above the OH stretching peak set which could be a direct observation of the hydrogen WP dynamics in the liquid water.

Anomalous and complex behaviors of liquid water are closely correlated to the dynamical rearrangements of the hydrogen-bond network (HBN). Our SQW MD simulation made it possible to directly view the WP dynamics in the liquid water, and have demonstrated that WP dynamics play an important role in the HBN dynamics. [2] For example, we found that WP dynamics accelerates the memory loss of the HBN and makes the HBN dynamics more complicated and manifold, indicating the presence of multiple timescale dynamics. We also found significant correlations between the WP dynamics and mesoscopic rearrangements of water molecules such as a cage breakout in liquid water.

We have recently extended the above method by expressing an electron (fermion) as a three-dimensional Gaussian WP basis function. The electron WP follows the perfect-pairing valence bond theory to appropriately treat the Pauli’s exclusion energy for many-electron systems. The developed method does not require any given model potential functions like the Lennard-Jones potential, and can treat the nuclear WPs describing the nuclear quantum effects without any perturbation. We already derived the extended potential functions which are necessary to establish this new MD method.[3] The extended potential functions let us discuss about the non-Born-Oppenheimer effects since the potentials were calculated by allowing both the nuclear and electron WPs to evolve freely.

On-the-fly free-energy reconstruction using logarithmic mean-force dynamics (LogMFD)

T. Morishita$^A$, S. G. Itoh$^B$, H. Okumura$^B$ and M. Mikami$^A$

$^A$ Nanosystem Research Institute (NRI), National Institute of Advanced Industrial Science and Technology (AIST), Japan
$^B$ Department of Theoretical and Computational Molecular Science, Institute for Molecular Science, Japan

A method for free-energy calculation based on mean-force dynamics (a fictitious dynamics on a potential of mean force) is presented [1]. The new method, logarithmic mean-force dynamics (LogMFD), utilizes a logarithmic form of free-energy to enhance crossing barriers on a free-energy landscape, which results in efficient sampling of rare events. Invoking a conserved quantity in mean-force dynamics, free-energy can be estimated on-the-fly without postprocessing. This means that an estimate of the free-energy profile can be locally made in contrast to the other methods based on mean-force dynamics such as metadynamics. The new method is benchmarked against conventional methods and its high efficiency is demonstrated in the free-energy calculation for a glycine dipeptide molecule.

Figure:
Free-energy profile $F(\psi)$ of a glycine dipeptide molecule as a function of the dihedral angle $\psi$ while constraining the dihedral angle $\phi$ at $-1.3962634$ (-80 degrees).

The LogMFD result (solid line) is compared with the thermodynamic integration result (filled circles). Also shown is the logarithmic form of $F(\psi)$ in the dashed line, indicating substantial reduction of the free-energy barrier.

Pebble Games on Fluctuating Networks in Glass-Forming Liquids: Implications for Slow Structural Relaxation

Yasushi TAKÉUCHI

Hinode Science Center, National Astronomical Observatory of Japan

The high abilities to form glasses of various inorganic materials, viz. silica (SiO$_2$), have their origins in network structures. Three-dimensional random networks percolate infinitely in liquid or vitreous silica. These structures cause slow structural relaxations, and their behaviors such as long shear relaxation times depend strongly on the degrees of connectivity in networks. These structures undergo transformations under high pressures, and thereby structural relaxations are affected. Highly-connected network liquids, viz. silica, especially display various enigmatic behaviors, such as decreasing shear viscosities under high pressures [1,2]. These enigmatic behaviors indicate the reduced connectivities in infinitely-percolating networks under high pressures. This reduction is ill identified, however, because, in a well-studied framework of the percolation theory, insights into internal structures of infinitely-percolating networks are hardly obtained.

In this work, internal structures of infinitely-percolating networks in glass-forming liquids are studied, by generating these networks from molecular dynamics (MD) simulations on highly-connected network liquids such as SiO$_2$ and Na$_2$O·2SiO$_2$, and then applying the algorithm of a “pebble game” to them. The pebble game algorithm was proposed in Thorpe, Jacobs and their coworkers’ studies on the percolation of rigidity to undergo glass transitions [3,4]. Besides its exactness in two dimensions [4], no rigorous extension of this algorithm is proven in three dimensions [5]. Recent works show that, nevertheless, the pebble game algorithm applies for three-dimensional networks such as proteins [6,7].

Applying the pebble game algorithm in MD simulations on glass-forming liquids, infinitely-percolating networks are decomposed into rigid or flexible domains. Their fluctuations in space and time to induce slow structural relaxations are traced by carrying out pebble games sequentially on the MD-generated ensembles. The results of these computations reveal that, even without the breakup of infinitely-percolating networks, high-pressure transformations of their rigid or flexible domains induce the decreasing shear viscosities.

Phase transition in peristaltic transport of granular particles

Naoki Yoshioka and Hisao Hayakawa
Yukawa Institute for Theoretical Physics, Kyoto University

Peristalsis is a progressive wave of area contraction and expansion in a tube. Transport due to the peristaltic motion of a tube is one of the main transport mechanisms in biological systems such as the esophagus, small intestines, ureter, and so forth [1]. Peristaltic transport is also found in the pumping of fluids, known as peristaltic pumps. While the study of peristaltic transport of fluids has a long history [1], there are few studies on the peristaltic transport of particles [2, 3]. Especially, the peristaltic transport of dense particles has never been studied.

We study flows of dissipative particles driven by the peristaltic motion of a tube using the discrete element method [4]. A transition from a slow “unjammed” flow to a fast “jammed” flow is found through the observation of the flow rate at a critical width of the bottleneck of a peristaltic tube. The jammed flow is characterized by the stationary value of flow rate $J_{st}$ is almost equal to $Nc/L$, where $N$ is the number of particles inside the tube, $c$ is the phase velocity of the peristaltic motion, and $L$ is the length of the tube. In order to determine the value of the critical width, we observe the time when the instantaneous value of the flow rate transits from $J < Nc/L$ to $J \sim Nc/L$ in the jammed flow phase. It is found that the average and fluctuation of the transition time, and the peak value of the second moment of the flow rate exhibit power-law divergence near the critical point and that these variables satisfy scaling relationships near the critical point. The dependence of the critical width and exponents on the peristaltic speed and the density is also discussed.

Figure 1: (a) Sequential snapshots of the simulation. (b) Snapshot of stationary state in jammed flow phase. (c) Time evolutions of the normalized flow rate with various widths of bottlenecks.

Atomic force microscopy simulation by MD/continuum coupling method

Yasuhiro Senda A, Nobuyuki Imahashi A, Shuji Shimamura A
Janne Blomqvist B, and Risto Nieminen B

A) Yamaguchi University, Japan
B) Aalto University, Finland

We have performed atomic force microscopy (AFM) simulation to clarify microscopic mechanism of atomic imaging of AFM experiment. Macroscopic motion of cantilever in AFM experiment is described by the continuum model and the atomistic interaction between the probe and surface is calculated by the molecular dynamics (MD) method. Atomic model and continuum model are connected by MD/continuum hybrid method developed by our group[1,2]. In this paper, we propose a simple AFM model, in which the probe and surface are consisted of Lennard-Jones atoms and the oscillation of cantilever is described by one-dimensional spring dynamics. The frequency of cantilever shifts when cantilever is approaching to surface and the energy dissipation from cantilever to atoms on the surface is found. These behaviors are consistent with the AFM experiment.

P-7

Origin of “super rebounds” in nanoclusters collision

Hiroto Kuninaka
Faculty of Education, Mie Univ

Dynamics of nanoclusters are extensively investigated from both scientific and technological interest. There are many numerical studies on cluster-cluster and cluster-surface collisions based on the molecular dynamics simulation, where we can observe variety of rebound processes for such systems caused by the competition between the attractive interaction and the repulsive interaction of two colliding bodies.

We carried out the molecular dynamics simulation of colliding thermally activated modified Lennard-Jones clusters to investigate the impact phenomena and found the existence of the ”super-rebound” in which the restitution coefficient is larger than unity [1]. Recently, it has been reported that such a rebound can be observed in a molecular dynamics simulation of a collision of Cu nanoparticles on a rigid wall [2]. However, the mechanism to appear the ”super rebounds” is still unclear.

We numerically investigate the mechanism of super rebounds for head-on collisions between nanoclusters from the molecular dynamic simulations of Lennard-Jones clusters [3]. It is confirmed that the temperature and the entropy of the nanoclusters decrease in the super rebounds by our molecular dynamics simulations. We will report that the initial metastable structure plays a key role for the emergence of the super rebounds. This work is the collaborative work with Hisao Hayakawa (YITP, Kyoto Univ.).

Hierarchical heterogeneous dynamics in supercooled liquids: vibration modes and configuration changes

Takeshi Kawasaki\textsuperscript{A}, Hayato Shiba\textsuperscript{B}, and Akira Onuki\textsuperscript{A}

\textsuperscript{A)} Department of Physics, Kyoto University, Kyoto 606-8502, Japan
\textsuperscript{B)} Institute for Solid State Physics, University of Tokyo, Chiba 277-8581, Japan

For understanding dynamic heterogeneities of glassy systems, we constructed the new theoretical schemes of bond-breakage, with comparing to those of four-point correlation functions. In the bond-breakage scheme, we introduce the dynamic structure factor $S_b(q, t)$ and the susceptibility $\chi_b(t)$ to obtain the spatial correlations of configuration rearrangement. Here attains a maximum at $t_b^{\text{max}}$ as a function of time, where the fraction of the particles with broken bonds is about 1/2. In the four-point scheme, treating the structure factor $S_4(q, t)$ and the susceptibility $\chi_4(t)$, we detect superposition of the heterogeneity of bond breakage and that of thermal low-frequency vibration modes. While the former grows slowly, the latter emerges quickly to exhibit complex space-time behavior. In two dimensions, the vibration modes extending over the system yield significant contributions to the four-point correlations, which depend on the system size logarithmically. A maximum of four point susceptibility $\chi_4(t)$ is attained at $t_4^{\text{max}}$, where these two contributions become of the same order. As a result, $t_4^{\text{max}}$ is considerably shorter than $t_b^{\text{max}}$ \cite{1}. Furthermore we investigate the close correlations between configuration changes caused by string-like jump motions on long timescales and thermal vibrational motions on short timescales \cite{2}.

\cite{1} H. Shiba, T. Kawasaki, and A. Onuki, \textbf{Phys. Rev. E} (accepted),
\cite{2} T. Kawasaki, and A. Onuki, (submitted).
Vapor-liquid coexistence of water in nanocylinder: a molecular dynamics simulation approach

Toshiki Mima A, Yuta Yoshimoto A, Ikuya Kinefuchi A, Akinori Fukushima B, Takashi Tokumasu B, Shu Takagi A, and Yoichiro Matsumoto A

A) Department of mechanical engineering, University of Tokyo, Bunkyo-ku, Japan
B) Institute of fluid science, Tohoku University, Sendai-shi, Miyagi, Japan

Molecular dynamics simulation was conducted in order to investigate the vapor-liquid phase equilibrium of the water molecules in nanopore. In this research, the Lennard-Jones energy parameter between a water molecule and an atom of nanopore was optimized so as to model the wettability of the carbon material in the fuel cell, that is, contact angle. The TIP4P/2005 as the model of a water molecule was used; this model reproduces well the vapor-liquid coexistence line[1]. All of the systems were equilibrated by Nosé-Hoover constant temperature algorithm. The electrostatic interaction between water molecules was calculated through smooth particle mesh Ewald method. First, we equilibrated a water plug in the single-wall atomistic nanocylinder as a model of nanopore in the fuel cell. Water molecules burst from an interface of the water plug in equilibration. Then, the equilibrium densities both in dense and dilute region were sampled over 1 ns.

The vapor-liquid equilibrium densities are shown in Fig. 1. The coexistence line shifts compared with the one in bulk condition[1]. This result is comparable with the one reported by Srivastava[2]. Density profile, chemical potential profile and further results will be presented in the poster session.

Figure 1. Vapor-liquid equilibrium densities of water in nanocylinder (triangle). Bulk result was also plotted as reference (circle).

Monte Carlo Simulations of Short Chain Branched Polyolefins: Structure and Entanglements

Krzysztof Moorthi A, Kazunori Kamio B, Javier Ramos C and Doros N. Theodorou D

A) Materials Science Laboratory, Mitsui Chemicals, Inc., Sodegaura City, Japan
B) MC Analysis and Consulting Service, Sodegaura City, Japan
C) Department of Macromolecular Physics, IEM CSIC, Madrid, Spain
D) Department of Materials Science and Engineering, National Technical University of Athens, Athens, Greece

The effect of higher α-olefin comonomer on physical properties of short chain branched (SCB) polyethylene (PE) melts at 450 K has been studied using connectivity altering Monte Carlo method [1]. The calculated chain dimensions per molecular mass scale with backbone weight fraction, $\phi$, as $\langle S^2 \rangle/M \sim \phi^{1.27 \pm 0.03}$ for the radius of gyration $S$, and $\langle R^2 \rangle/M \sim \phi^{1.27 \pm 0.03}$ for the end-to-end distance $R$, in very good agreement with the experiment-based result [2] $\langle R^2 \rangle/M \sim \phi^{1.30}$.

The entanglement tube diameter, $a_{pp}$, computed for SCB melts scales as $\langle a_{pp} \rangle \sim \phi^{-0.46 \pm 0.01}$, which is close to the result for model concentrated ($\langle R^2 \rangle=$const) PE solutions created by deleting randomly chosen chains from equilibrated melt configurations of linear PE ($\langle a_{pp} \rangle \sim \phi^{-0.41 \pm 0.01}$). The latter result agrees very well with the scaling based on rheological experiments [3] on concentrated hydrogenated polybutadiene (HPB)/C_{24}H_{50} solutions at 413 K ($\langle a_{pp} \rangle \sim \phi^{-0.45}$). The tube diameter in model athermal PE solutions scales as $\langle a_{pp} \rangle \sim \phi^{-0.6 \pm 0.03}$ in excellent agreement with the scaling based on the neutron spin echo experiments [4] on athermal HPB/C_{19}D_{40} solutions at 509 K ($\langle a_{pp} \rangle \sim \phi^{-0.5}$). The computed scaling relationships for both SCB melts and model PE solutions are close to the binary contact model [5] ($a_{pp} \sim \phi^{-1.27}$) and disagree with the packing model [6].

Free energy analysis for the placement of transmembrane proteins in a lipid bilayer

Tomoko Mizuguchi A,B, Nobuyuki Matubayasi A
A) Kyoto University
B) Institute for Molecular Science

The configuration of a transmembrane protein in a lipid-membrane environment plays important roles in the functions of bio-related membranes and the elaboration of drug-delivery systems. It is determined by the cooperation and/or competition of the intra- and intermolecular interactions among the protein, lipid, and water molecules at atomic resolution. An all-atom analysis is thus desirable to identify the key factor determining the binding mode of protein into membrane.

In the present work, we examined different configurations in the path for the protein flip-flop motion in a model membrane system using all-atom molecular dynamics simulations with explicit solvent and to estimate the free energy barrier of the process. The flip-flop motions of proteins and peptides have been observed in several experimental studies [1,2]. The purpose of the current work is to give a detailed theoretical analysis of the flip-flop process. The free energy was calculated by using the energy-representation method [3]. This method is a statistical-mechanical theory of solutions and expresses the free energy of protein binding into membrane in terms of energy distribution functions. Within the framework of the method, in particular, the free energy can be decomposed into the contributions from lipid and water. Through the decomposition, the roles of lipid and water are separately revealed, and the dominant interaction to determine the protein configuration is identified.

Controlling of Swimming in Granular Bed

Takashi Shimada
Department of Applied Physics, Graduate School of Engineering, The University of Tokyo

Inspired by some lizards those live in deserts and can swim in sand bed, here we address a problem: How to swim in sand? From a systematic event-driven MD simulation with a simple model swimmer which consists of only two hard disks, we found that essentially there exist two different optimum frequencies for the motion of swimming. One optimum frequency gives the fastest translational velocity. Another optimum frequency, which is about only ten times smaller than the former one, maximizes the energy efficiency of the swimming [1]. Those frequencies correspond to typical time scale of “evaporation”, fluidization, and solidification of granular bed.

The remaining problem is the controlling of the direction. To consider this problem, we next simulate a simple three-dimensional swimmer with rudder (Fig. 1). We find that certain angle and size of the rudder gives optimum turning, in terms of its curvature and accuracy. The mechanism to have those optima will be discussed.

Figure 1: A snapshot of the simulation system. Our model swimmer consists of the three large balls connected with the beam. Other small particles show the size of the surrounding granular grains (for visibility, its only a small part of is drawn).

We used Wang–Landau sampling [1] with inventive Monte Carlo moves [2] to simulate the physical behavior of a hydrophobic-polar (HP) lattice protein model [3] confined between two attractive, parallel surfaces. Three types of surfaces, namely, surfaces that attract: (a) all monomers; (b) only H monomers; or (c) only P monomers, have been considered. After obtaining the densities of states, we then found the thermodynamic and structural quantities, e.g., specific heat, number of surface contacts and number of hydrophobic interaction pairs. A few conformational “transitions”, e.g., debridging process, “flattening” of adsorbed structure and hydrophobic core formation, can be identified based on an analysis of these quantities. Depending on the surface types, these transitions take place at different temperatures, while the ground state configurations show structural variations. These scenarios are confirmed by snapshots of typical states of the systems.

Figure 1: Thermodynamic and structural properties of 36mers confined between two surfaces that attract all monomers.

Tight-binding molecular dynamics with Fermi operator expansion: application to vacancy defects of silicon

Sasfan Arman Wella A,B, Makoto Nakamura A, Masao Obata A, Suprijadi B, Tatsuki Oda C

A) Grad. School of Natural Sci. and Tech., Kanazawa University, Kanazawa 920-1192, Japan
B) Faculty of Mathematics and Natural Sciences, Institut Teknologi Bandung, Indonesia
C) Institute of Science and Engineering, Kanazawa University, Kanazawa 920-1192, Japan

Silicon has great economic and technological importance, even nowadays when the limitation of silicon electronic device is claimed. The defects in crystal silicon have been argued and properties of vacancy have interested researchers for a long time in the view point for controlling the defect in electronic devices. The defect has almost been created in the crystal growth from the liquid state. In order to investigate silicon system, we have been implemented the tight-binding molecular dynamics (TBMD)1, which is widely used to investigate dynamical properties of clustering atoms and disordered material and, especially, expected to be able to reveal processes of bond breaking or re-bonding. The present work employed the Fermi operator expansion method2,3 which has an order-\( N \) property in the computational cost and is suited in massively parallelized computation. Previously, the TBMD with a Fermi operator expansion4 has been developed and successfully applied to liquid carbon. In the present work we have installed the tight-binding potential of silicon5 and applied to silicon defects, especially vacancy defects in silicon. This potential has been obtained by fitting from experimental reference data and ab initio data. Using this potential, the TMBD code developed has been checked in silicon crystal, point defect formation energies, etc. The crystal configuration for checking varies among the systems of 64, 216, 512, and 1000 atoms. We have also checked the expansion condition of Fermi operator; the smearing width, the maximum order of expansion polynomials. The testing shows the good results, compared with the ab initio result6. In the presentation other results in testing and efficiency of parallel computation will be discussed.

GPGPU simulations of 2D lattice neutral models in ecology

Takeshi Oura A,B and Kei Tokita A,B,C

A) Cybermedia Center, Osaka University
B) Graduate School of Science, Osaka University
C) Graduate School of Frontier Biosciences, Osaka University

Hubbell’s neutral model of biodiversity is known as an ecological model which predicts specie abundance distributions [1]. While the model has been mainly analyzed by mean-field theory, to consider more realistic situations we studied 2D lattice neutral model in ecology by using general-purpose computing on graphic processing units (GPGPU). A main result concerning the computational physics is that the processing time per site by GPU (nVIDIA Tesla C2050) is much shorter than the one by CPU (Intel Xeon W3530 2.8GHz) (Figure 1). In special, for the system size $L \times L > 512 \times 512 = 262144$ the GPGPU version is more than 100 times faster than the CPU version. Processing time of GPGPU is maximally 370 times higher than CPU’s. In the talk, we also report results compared with multi-CPPs (MPI and openMP), multi-GPPUs and NEC SX-9 supercomputer. Ecological significance of the GPGPU simulations and the lattice neutral model is also reported.

Figure 1: Processing time per site $\frac{T}{L^2}$ vs. the system size $L^2$.

Symplectic Time Integration of Transformed Canonical Variables

Atsushi M. Ito
National Institute for Fusion Science.

The symplectic time integrator is the method most often-used for the time evolution of the equations of motions in molecular dynamics (MD). The reason for this is that the symplectic time integrator has the following two advantages: one is that the Hamiltonian of the system, which is a total energy, is conserved for long steps of time evolution, and the other is that the phase volume (measure) of the system is preserved during time evolution. The former is useful for long time MD simulations, for example long time problems in statistical physics and real atomic simulations aimed at the micro-seconds phenomena of nano-material. The latter is important for the accurate estimation of amount of statistics such as ensemble average.

By the way, in MD simulation, the methods to control temperature and pressure had been well developed to advance statistical physics, and they are applied to the simulation in the nano-material science. Among them, since the Nose-Hoover and Nose-Poincare thermostat methods and the Andersen barostats methods are constructed as Hamiltonian systems, the symplectic integrators of these methods had been developed. The presence of the symplectic integrator was helping to spread these methods. Here, if the problem of the symplectic integrators for these methods is picked up daringly, it is that we must treat the canonical variables, which is called “the variables in virtual system”, during the time evolution of MD simulations. This constraint is a bother because usually observed quantities are functions only of the transformed variables, which is called “the variables in real system”.

In the present paper, therefore, the symplectic integrators for non-canonical variables transformed from canonical variables are proposed. General rule of the symplectic integrator in terms of the transformation of canonical variables are considered. Moreover, as concrete examples, the symplectic integrators for the Nose-Poincare thermostat, Andersen barostat and Nose-Poincare-Andersen thermo-barostat methods are illustrated.

Many kinds of symplectic integrators had been already developed. Then, let’s discuss the novelty of the present approach.
**Diffusion Constant in the Totally Asymmetric Simple Exclusion Process**

Shahla Nikbakht, Ian McCulloch, Dirk P. Kroese  
*School of Mathematics and Physics, The University of Queensland, QLD 4072, Australia*

We found Matrix Product State as a reasonable approach to describe the probability distribution of a classical stochastic system. We adapt TEBD algorithm—which is used for simulation of one dimensional quantum systems—to study the behavior of a tagged particle in the asymmetric simple exclusion process (ASEP). We investigate un-equal time correlations and particularly, the quantity which is related to such a correlation, called diffusion constant which represents the fluctuations in the distance travelled by the tagged particle.