SYNOPSES OF
SCIENCE AND ENGINEERING PAPERS
GRADUATE SCHOOLS OF

- SCIENCE AND ENGINEERING -
- FUNDAMENTAL SCIENCE AND ENGINEERING -
- CREATIVE SCIENCE AND ENGINEERING -
- ADVANCED SCIENCE AND ENGINEERING -

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Study of Fundamental Aspects of Transport in Mesoscopic Systems

by

Shigeru AJISAKA

Understanding the macroscopic transport from microscopic point of view is a central topic of physics. Development of nanoscale devices in particular reveals unconventional transport. As such study of transport in mesoscopic systems holds significant value both in fundamental theory and technologies. Since mesoscopic systems are strongly coupled with environments, their understanding at nonequilibrium states requires global features of total systems including environments. Though analytical frameworks have been developed, there is still no consensus on how to handle nonequilibrium states. Therefore, analytical studies of individual systems can contribute to the development of the fundamental theory of nonequilibrium systems. In this paper, we choose two conceptually simple models from classical and quantum systems and study their transport in detail.

In part I, we study a one-dimensional electron-phonon model coupled to a pair of reservoirs. As phase transition induces marked changes in materials such as conductivity and susceptibility, it is of great importance in both theoretical and experimental aspects. However, the roles of the current or chemical potential have in phase transition are not well understood. As a representative example of quantum systems exhibiting phase transition, we study a nonequilibrium steady state (NESS) of the spinless Takayama Lin-Liu Maki (TLM) model coupled with two free fermionic reservoirs (an open TLM model). This model shows the spontaneous lattice distortion, and we employ the averaged lattice distortion as an order parameter. Using the C* algebra method, NESS of electronic state in an effective potential is constructed, where the lattice distortion is replaced by a time-independent averaged value. Then, self-consistent equation for the lattice distortion is studied in the case of isotropic lattice distortion, solitons and polarons. It is shown that the amplitudes of the all three solutions do satisfy the same self-consistent equation. In addition, polarons are required to satisfy another equation which determines the width of polarons. Since no general thermodynamic criterion is available for discussing the stabilities of NESS, we study the phase stability based on the linear stability of the adiabatic evolution equation for an isotropic order parameter. We also point out that constant-voltage case and constant-current case should be distinguished to determine the stability.

It turns out that the order parameter is a multi-valued function of the voltage in constant-voltage case, thus, both first-order and second-order phase transitions are possible. On the other hand, the order parameter is a monotone-decreasing single-valued function in constant-current case, thus, only second order phase transition is possible. In this sense, the current is a more natural parameter than the voltage to control the system. Moreover, it is shown that a negative differential conductivity regime arises at low temperatures. In our study of polarons, we obtained temperature-dependent lower and upper thresholds of the current, between which polarons are possible. Since polarons are not possible in equilibrium spinless-TLM model, this phenomenon can be considered as an example of dissipative structures in microscopic systems. The results are compared with those of the XXZ chain obtained by Lindblad equation and of the nonequilibrium superconducting phase induced by excess quasiparticles. Then, on the basis of the similarity of mean-filed approximation of an open TLM model and an open 1D extended Hubbard model, our results are also compared with the experimental results for some

θ -type BEDT-TTF organic conductors. We conclude that the current-voltage characteristics and the suppression of the charge order by the current observed in the experiment qualitatively agree with those of an open TLM model. We also discuss the thyristor effect observed in the experiment.

In part II, we study stable and unstable manifolds of a two dimensional area-preserving nearly integrable system exhibiting bifurcation. In classical dynamics, hyperbolic systems as well as the integrable systems are well understood. In contrast, our understanding of systems whose phase space is filled with both chaotic regions and quasi-periodic orbits is still incomplete. Since homoclinic structure generates chaotic regions in phase space, co-existence of chaotic orbits and quasi-periodic orbits is typical in Hamiltonian systems. Therefore, understanding transport in such systems is crucial. Moreover, this subject is also important as a fundamental problem of statistical physics because an ergodic property is not satisfied in such systems. In particular, bifurcations drastically change transport properties of the phase space, understanding the homoclinic (heteroclinic) structure of systems exhibiting bifurcation is imperative. As a representative example of systems exhibiting bifurcation, we study the Harper map. The Harper map is one of the simplest examples exhibiting a bifurcation of the topological structure in the separatrix (reconnection), and we mainly focus on our attention on the reconnection. Thus we closely examine the parameter dependence of stable and unstable manifolds in the Harper map. Though the importance of the homoclinic (heteroclinic) structure has been known qualitatively since Poincare, the quantitative approach to homoclinic (heteroclinic) structure has been difficult until only recently. Since perturbation theory cannot be applied to chaotic orbits, including those related to stable and unstable manifolds, it is of great importance to develop methods to approximate phase space structure more accurately. In the 1980's, this was partially resolved by Lazutkin et. al.. They developed the method of the asymptotics beyond all orders (ABAO), and successfully derived the asymptotic expansion for an exponentially small quantity which characterizes the homoclinic (heteroclinic) tangles. Then, Gelfreich et. al. showed that the same results are obtained using the Borel transformation. The key idea of these methods is extending the time coordinate to the complex time domain, and studying the behavior of the perturbative solutions near their singularities. These methods are now known to be some of the most powerful tools available for the analytical study of homoclinic (heteroclinic) tangles. The Harper map involves two parameters. One of them corresponds to the time step; the map approaches the integral limit when the time step goes to zero, thus this parameter is used as a perturbation parameter. The other controls phase space structure, and reconnection is induced by changing this parameter. Since the errors of the perturbative solutions diverge at the singular points of the perturbative solutions, we approximate the true solutions in those regions through the inner solutions. By approximating the true solutions through the perturbative solutions and the inner solutions in the complex time domain, the asymptotic series of the stable and unstable manifolds are obtained with exponentially small errors for the whole real time domain. We point out that the choices of the initial time of the perturbative solutions relate to the coefficient of the asymptotic series for the stable and unstable manifolds. It only occurs in systems whose perturbative solutions have more than one sequence of singular points in the complex time domain, such as the Harper map, and the initial conditions should be chosen carefully when discussing reconnection.

The so obtained approximate solutions of the stable and unstable manifolds are compared with the numerically obtained manifolds. We conclude that the approximate solutions obtained by asymptotic analysis agree with the numerically obtained solutions even over long periods of time. The time domains in which the approximate solutions effectively reproduce the original manifolds can be expanded by taking the higher order term of the Borel summation method (or equivalently the ABAO method). We further show that when the system is close to reconnection, the stable and unstable manifolds get new oscillation, which is considered to be the precursor of a heteroclinic tangles after reconnection. Because of this, some stochastic regions are combined and the topology of the phase space is drastically changed.

ACCELERATIONS OF AB INITIO MOLECULAR SIMULATIONS AND APPLICATIONS TO HYPERVALENT COMPOUNDS

by

Teruo ATSUMI

Theoretical calculation methods which describe chemical phenomena are broadly classified into two categories, i.e., ab initio calculations as typified by the molecular orbital (MO) method and density functional theory (DFT), and molecular simulations as typified by the molecular dynamics (MD) and Monte Carlo (MC) simulations. The ab initio calculation can yield electronic wave functions, which are essential to describe chemical bonds, by solving the Schrödinger equation. Because most of the ab initio calculations are based on the Born-Oppenheimer (BO) approximation, it is difficult to directly obtain the dynamical information of nuclei. On the other hand, the molecular simulations can describe nuclear motion by using an empirical potential which cannot represent the formation and/or dissociation of chemical bonds in the quantitative accuracy.
Ab initio simulations are the hybrid methods of the above two methods, and have been widely used. The ab initio molecular dynamics (AIMD) simulation, which is the combination of the ab initio calculation and the MD simulation, can directly trace the trajectory with the chemical bond formation/dissociation. The ab initio Monte Carlo (AIMC) simulation, which is the combination of the ab initio calculation and the MC simulation, can obtain thermal distribution of nuclei, and is also used for searching the local minima on the potential energy surface. However these hybrid methods have the disadvantage of high computational cost which is caused by the repetition of the ab initio calculation.
Thus, this thesis aims for the acceleration of ab initio simulations. The author developed two acceleration methods. Furthermore, the AIMC simulation was applied to the bond switching equilibration reaction with hypervalent bond.

This thesis consists of six chapters, which are summarized as follows.

Chapter 1 described the general introduction, or the background, of this study. The MD, MC, AIMD, and AIMC simulations were introduced, and the concept of hypervalent bond was given.

In Chapter 2, the acceleration method for the AIMD simulation, which is named Lagrange interpolation molecular orbital (LIMO) method, was introduced. The basic idea of the LIMO is the improvement of the initial guess of molecular orbitals (MOs) for the self-consistent-field (SCF) procedure, which provides a BO potential energy and is the main bottleneck of the AIMD simulation. The LIMO predicts the converged MO at the next MD step by the linear combination of the converged MOs at several previous MD steps. By using the predicted MO as the initial guess at next MD step, the number of SCF iterations needed to achieve convergence is reduced. The linear combination coefficients are determined by the Lagrange interpolation (LI) polynomial technique introducing the information of the physical time of the MD simulations. Additionally, taking into account the crossing and/or mixing of MOs leads to orbital invariant formulation for the LIMO

method. The author proposed a simple method for determining the optimal degree of the LI polynomial, which corresponds to the number of previous steps. Numerical tests confirmed that the proposed method is both effective and feasible for AIMD simulations.

In Chapter 3, another acceleration method for the AIMD and AIMC simulations and geometry optimization, which is named least-square molecular orbital (LSMO), was proposed. The LSMO method is based on the idea of the LIMO in Chapter 2. A major difference from LIMO is determination of the linear combination coefficients. LIMO method determines the coefficients by the LI technique with the time information and thus cannot be straightforwardly applied to the AIMC simulation and geometry optimization for the lack of the time information. On the other hand, LSMO method determines the coefficients by the least-square technique with the geometrical information. The author checked the performance of the LSMO method and confirmed the effectiveness and feasibility in the AIMD and AIMC simulations, and geometry optimization.

In Chapter 4, the author assessed the mechanism of bond-switching of 1,6-diazadihydrothio (6aS) pentalene (10-S-3) systems and corresponding oxygen analogues. Geometries and energetics were examined along unimolecular and bimolecular reaction paths by taking into account solvent effects. It was clarified that the unimolecular reactions cannot proceed due to the high energy barriers. On the other hand, the bimolecular processes in neutral and acidic conditions can be accomplished for the sulfur compounds, not for the oxygen ones. The differences of the reactivities between the sulfur and oxygen compounds were found to be due to the difference of the stability of the symmetric intermediates with a hypervalent three-center four-electron (3c-4e) bond.

In Chapters 5 and 6, the author investigated hypervalent bonding systems of the pentalene skeleton with central atoms X of group 14-16 and period 2-5 elements. In Chapter 5, the bond energies of the O-X and N-X hypervalent 3c-4e bonds are estimated. Furthermore, the relationships between the bond-switching equilibration reactions and the stabilities of the hypervalent bonding intermediates were examined. In Chapter 6, the stabilities of starting materials and possible intermediates during bond-switching equilibration were considered.

Chapter 7 described the general conclusion of this thesis.

STUDY ON LONG-TERM DIMENSIONAL STABILITY OF LIGHT WEIGHT AND HIGH PRECISION CFRP MIRROR

by

Yoshihiko ARAO

Since CFRP(Carbon Fiber Reinforced Plastics) has low density and low thermal expansion, some experiments to design -ased mirror by CFRP have been conducted The design method and density of the material determine the limit performance of the space-based telescope, because there is a weight limit of the rocket. In order to improve the resolution of the telescope drastically, the accurate design using the materials that are light weight and low thermal expansion is investigated.

The conventional materials for the telescope were Ultra-Low-Expansion glass or beryllium. These material has zero thermal expansion only around cryogenic temperature. What is more, a toxicity of beryllium during processing is problem. Comparing above materials, CFRP has lower density and zero thermal expansion in wide temperature range. Therefore, the accurate design using CFRP is expected.

Mirrors are used to reflect radiation; hence their overall figure and surface smoothness must be adequate and stable for the wave length of interest. The requirements for diffraction limit primary optics are the following: (1) Surface Accuracy ($<\lambda/20$ RMS), λ (623nm) is the wave length of interest ranging from a submicron for UV and optical system. (2) Stability (surface displacement and/or deformation $<< \lambda$), this includes long term temporal and thermal stability. It was reported that CFRP mirror deformed about 10μmRMS with time. This micron deformation is critical problem for designing accurate mirrors. The deformation mechanism has not been clarified and an there is no design answer for improving the accuracy of mirror. The deformation against external load is predictable, since the bending stiffness of CFRP structures can be calculated. However, the time-dependent deformation is not unpredictable. To make breakthrough in developing the performance of the telescope by applying CFRP, quantifying the amount of time-dependent deformation and clarifying the mechanism of the micron deformation are prime task.

In this study, we investigated the time-dependent deformation of high-elasticity CFRP which is used for precise structures due to its high modulus. We categorize time-dependent deformation of CFRP as follow: ①deformation caused by moisture absorption ②thermal deformation ③creep deformation ④deformation due to the physical aging of a polymer ⑤deformation caused by internal stress relaxation. Moreover, out-of-plane deformation does not occur with moisture absorption or temperature change as long as ideal symmetric laminates. However, as described above, the out-of deformation was generated by temperature change, despite of symmetric lay-up. Therefore, the symmetric properties cannot be obtained even if the layer stacked symmetric against center plane. The deviation of fiber and ply angle misalignment might by one of the factor that generate asymmetric property of symmetric laminates. We should discuss the deformation considering these factors. We constructed the finite element CFRP mirror model considering the ply

angle misalignment. By performing the time-dependent deformation analysis of CFRP mirror considering errors, we specified the principal factor of the deformation. The purpose of this study is to suggest the accurate design method of CFRP structure thought the results of this investigation.

At first, we examined the deformation of symmetric cross-ply laminate. The deformation of symmetric laminate has never discussed before, since the deformation of that is quite small. We devised the experimental set-up to obtain specimens figure with high accuracy. From experimental results, it was verified that the symmetric cross-ply laminates twist about 100μm order under hot and humid environment. In the analysis, the deformation by absorbing water was calculated considering the deviation of fiber and ply angle misalignment. Since ply angle misalignment exist in all layers, Monte Carlo method of which the ply angle misalignment was assumed to be random number was applied to investigated the deformation statistically. As a result of Monte Carlo simulation, it was clarified that the symmetric cross-ply laminate twist due to the ply angle misalignment, and deform into saddle shape due to the fiber deviation or scattering of material properties. The analytical results for ply angle misalignment correspond to the experimental results. By comparing the analytical results with experimental results, it was clarified that the accuracy of ply alignment is about $\pm 0.3°$ in this material system. This value is unavoidable value. When we design precise structure using CFRP, the accuracy of ply alignment must be considered. In this case, we have to take into account $\pm 0.3°$ of ply angle misalignment. We suggested the indicator for an accurate design considering the unavoidable error.

Based on above results, we performed time-dependent deformation analysis of CFRP honeycomb sandwich structures. The structure is composed of only CFRP. Surface sheet of the structure is quasi-isotropic CFRP laminate, and the surface sheet is bonded to honeycomb core using adhesive mat. To consider the ply angle misalignment, one of the surface layer of quasi-isotropic laminate was rotated about 1°. The material properties of honeycomb core were calculated theoretically. In this analysis, the calculation cost was reduced by replacing the honeycomb core with 3-dimensional solid element. The finite element model for honeycomb sandwich structure was constructed, and the time-dependent deformation analyses for moisture absorption, thermal change, creep, and matrix shrinkage caused by physical aging were performed, respectively. From analytical results, it was clarified that the deformation due to the moisture absorption or temperature change is greater that the deformation cased by other factors. The amount of the deformation depends on the height of core. We confirmed that 1m-class of general mirror (diameter: height= 6:1) deform within 1μmRMS under space environment.

We manufacture the CFRP mirror by way of trial. To reduce moisture absorption, the cyanate-based CFRP was adopted to the material of surface sheet and honeycomb core. The gel coating technique was conducted to create smooth mirror surface. Dimensional stability of CFRP mirror was evaluated by interferometer. Twisted surface figure was observed, and the accuracy of the surface was 180nmRMS. The micron level deformation can be guaranteed in this prototype, but there are some problems to achieve sub-micron level dimensional stable structure.