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EMBEDDED MICROCLUSTERS IN ZEOLITES AND CLUSTER BEAM SPUTTERING -- SIMULATION ON PARALLEL COMPUTERS

Progress Report

September 1992 - September 1993

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ANNUAL PROGRESS REPORT (September 15, 1992 - September 14, 1993)

PROPOSAL TITLE: Embedded Microclusters in Zeolites and Cluster Beam Sputtering - Simulation on Parallel Computers

GRANT NUMBER: DE-FG05-92ER45477

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EXECUTIVE SUMMARY

An optimal time-space multi-resolution approach has been designed to carry out large-scale molecular-dynamics (MD) simulations on distributed-memory MIMD (Multiple Instructions Multiple Data) machines. This approach involves highly efficient algorithms for long-range Coulomb forces and three-body interactions. Tests on Intel's 512-node Touchstone Delta machine at Caltech indicate that an MD time step for a covalent material with 4.2 million atoms takes only 5 seconds! This is the most efficient parallel implementation of the MD approach for real materials.

The multi-resolution MD approach has been used to investigate structural correlations in porous silica - an environmentally safe thermal insulator used in refrigeration, in passive solar energy collection devices, as a solid-state catalyst, and as an embedding material in optical switches. The important structural parameters such as the internal surface area and surface-to-volume ratio of pores, pore size distribution, fractal dimension, and the mean particle size have been calculated over a wide range of densities. The simulation results are in accordance with structural measurements.

Molecular-dynamics simulations have also been performed to provide a microscopic understanding of recent pioneering high-pressure experiments on silica glasses at the National Synchrotron Light Source at Brookhaven National Laboratory. The simulations reveal a structural transition to a new high-pressure amorphous phase with corner- and edge-sharing SiO_6 octahedra.

Parallel algorithms have also been designed for an *ab initio* quantum dynamics approach to materials simulations. The implementation on MasPar's 8,192-node SIMD (Single Instruction Multiple Data) machine achieves 64% of the peak performance. With this approach, we have investigated the nature of electron transport in materials. We have also developed a tight-binding MD approach to investigate the influence of orientational disorder on structural correlations and phonon spectra of C_{60} solid. The results are in excellent agreement with neutron-scattering measurements.

Currently, large-scale MD simulations ($\sim 10^6$ atoms) are being performed to investigate the relationship between structure, dynamics, and mechanical properties and the influence of environment, composition, and stress conditions on nanophase ceramics (Si_3N_4, SiC, TiO_2, and Al_2O_3), and on silicates, aluminosilicates, and zeolites.

RESEARCH ACCOMPLISHMENTS

This report summarizes our research accomplishments in materials simulations and high performance computing during the first year of DOE funding. The work reported here was carried out on parallel architectures (an 8,192-node MasPar 1208B, an 8-node Intel iPSC/860 system, a 64-cell iWarp machine, and a Silicon Graphics Power Center 4D/380VGX) in our Concurrent Computing Laboratory for Materials Simulations (CCLMS). (Figure 1 shows schematically the set up of CCLMS.) Multi-million particle atomistic simulations are being carried out on the 512-node Touchstone Delta machine. The next phase of this project will also utilize a 56-node Intel Paragon system which is being acquired with our latest infrastructure enhancement grant from the State of Louisiana.

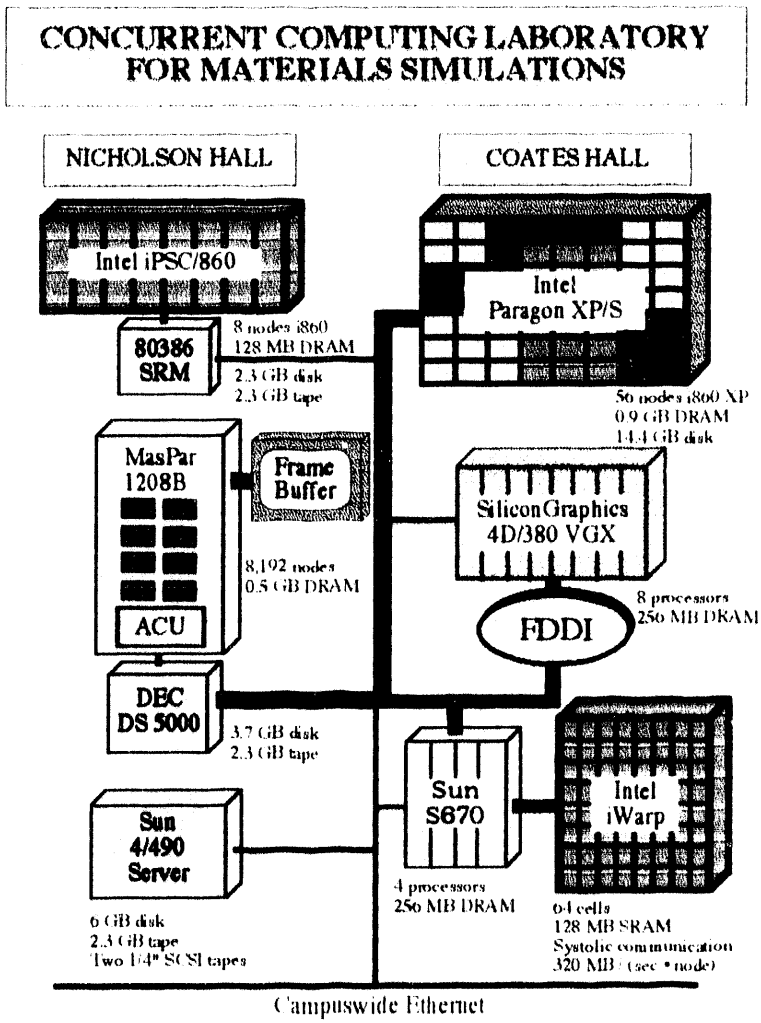

Figure 1: Computing facilities in the CCLMS' two parallel computing laboratories.

§1 Multi-million Particle Molecular-Dynamics Simulations on Parallel Machines

A variety of technologically important materials - for example, cluster-assembled nanophase materials, porous glasses, amorphous polymers - are composed of large-scale structural units, each consisting of 10^3 to 10^5 atoms which interact via long-range Coulomb and three-body covalent potentials. Condensed-phase simulations of these materials require large system sizes exceeding 10^6 particles.

Highly efficient algorithms have been developed to carry out these "Grand Challenge" materials simulations on parallel computers. The algorithms employ the divide-and-conquer strategy shown in Fig. 2 to reduce computations by several orders of magnitude. The long-range Coulomb interaction experienced by a particle is computed by partitioning it into two parts: 1) a near-field contribution due to direct interaction with particles in neighboring boxes; and 2) a far-field contribution due to distant charged regions. The near-field contribution can be computed efficiently with the linked-list scheme. The far-field contribution is calculated with recursive domain decomposition of the system and a truncated multipole expansion for interactions between distant charged regions. The multipole expansion of the potential due to charges in each subdomain are combined hierarchically in such a way that only O(N) operations are required.

For short-ranged two-body and three-body interactions, we have employed a multiple-time-step scheme (MTS) scheme in which the force on a particle is subdivided into primary, secondary, and tertiary components (see Fig. 2 (c)). A significant reduction in computation is achieved by exploiting different time scales of these force components. The primary forces arise from nearest neighbors and they are updated after every MD time step. Compared to primary interactions, the secondary and tertiary forces vary slowly and therefore they are updated after n_1 (~ 15) and n_2 (~ 120) time steps, respectively. Between updates, the secondary and tertiary forces are calculated from Taylor's series.

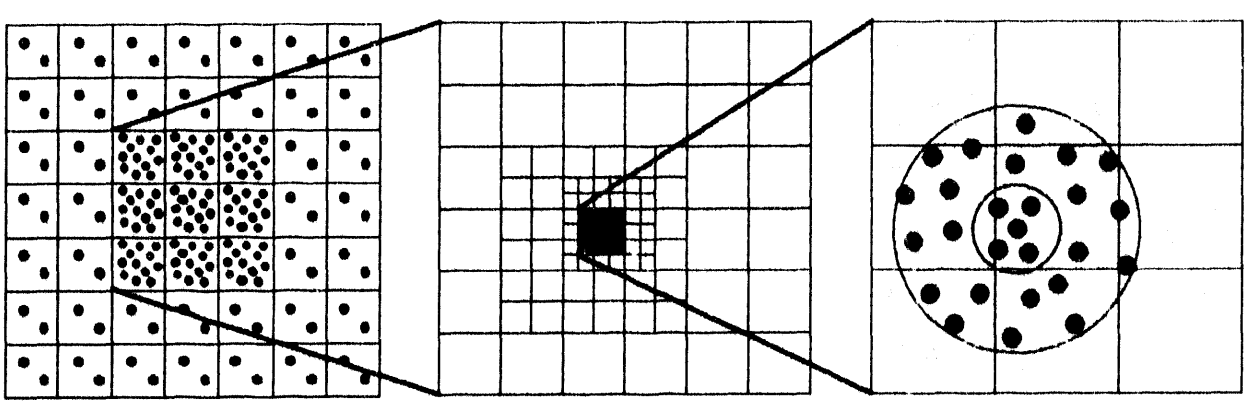

Figure 2: Multi-resolution in space. (a) Periodically repeated images of the original MD box. Replacing far images by a small number of particles with the same multipole expansion up to a certain order reduces the computation enormously while maintaining the necessary accuracy. (b) A hierarchy of cells used in the fast multipole method. (c) The near-field force on a particle (red) is due to primary (blue), secondary (green), and tertiary (gray) neighbor particles.

Figure 3 shows the overall performance of the multi-resolution MTS-MD approach on the 512-node Touchstone Delta machine. For a 4.2 million-particle silica glass, a single MD step takes only 4.84 seconds! The execution time scales linearly with the size of the system and the computation dominates the communication time. This is the most efficient implementation of the MD approach.

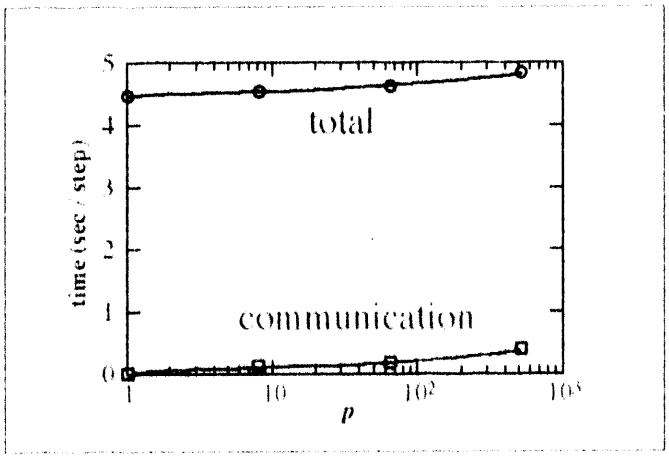

Figure 3: Execution time (circles) and communication time (squares) per MD time step for SiO_2. Here **p** is the number of nodes of the Touchstone Delta machine. The size of the system, N, increases as 8232 **p**. Because of excellent scalability of multi-resolution algorithms, the execution and communication times remain almost constant with **p** and N.

§2 Structural Transformation in Microporous Silica

Aerogel silica, a porous form of SiO_2 prepared by hypercritical drying of an alcoholic silica gel, is an environmentally safe material with a large thermal resistance which makes it a suitable alternative to chlorofluorocarbon (CFC)-foamed plastic in thermal insulation of commercial and household refrigerators. Scientists at Lawrence Livermore National Laboratory and Lawrence Berkeley Laboratory are investigating various other commercial uses of aerogel silica. These include passive solar energy collection devices, catalysis and chemical separation, and optical switches where porous materials are used as embedding frameworks for quantum-confined semiconducting microclusters.

From the technological standpoint, it is important to know the size distribution, the internal surface area and surface-to-volume ratio, and the interface texture of pores. Molecular-dynamics simulations were performed to determine these structural parameters over a wide range of densities, from 2.2 g/cm^3 to as low as 0.1 g/cm^3. Snapshots of atomic positions in Fig. 4 reveal a structural transition from the condensed amorphous phase to a low-density porous phase. The latter is a fractal network whose dimensionality decreases rapidly with a decrease in the density. The density dependence of the internal surface area is in good agreement with X-ray measurements.

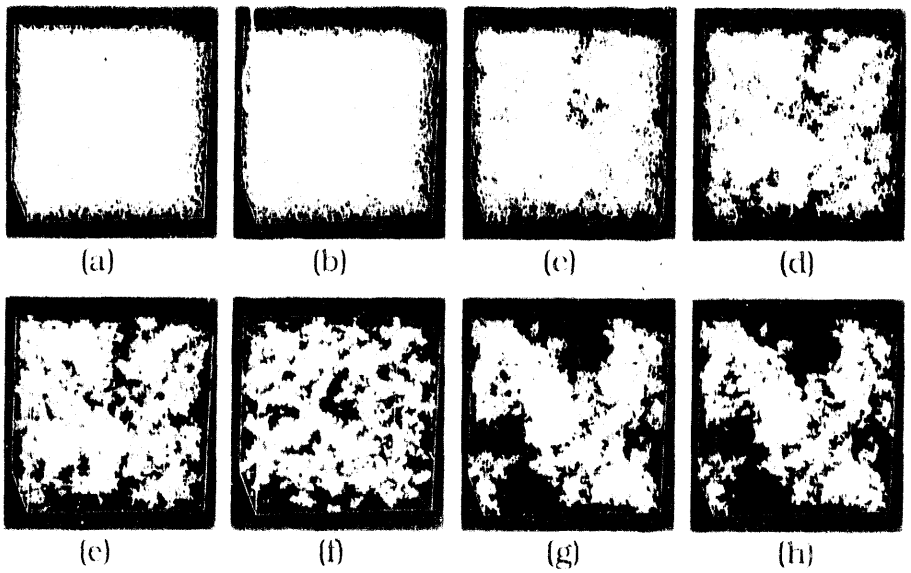

Figure 4: Snapshots of MD configurations showing Si-O bonds in room-temperature porous SiO_2 glasses at densities (a) 2.2, (b) 1.6, (c) 0.8, (d) 0.4, (e) 0.2, and (f) 0.1 g/cm^3. Here (g) and (h) are snapshots of systems with densities 0.2 and at 0.1 g/cm^3 at 1,000 K.

§3 Novel High-Pressure Phase of Amorphous Silica

Recent in-situ high pressure X-ray measurements at the National Synchrotron Light Source at Brookhaven National Laboratory revealed dramatic changes in the structure of amorphous silica. Molecular-dynamics simulations were performed to gain insight into the microscopics of structural changes at high pressures. Under normal conditions, amorphous silica is a disordered network of corner-sharing SiO_4 tetrahedra, see Fig. 5. However, at high pressures exceeding 40 GPa, the simulations reveal a new disordered network consisting of corner-sharing and edge-bonded SiO_6 octahedra, see Fig. 5

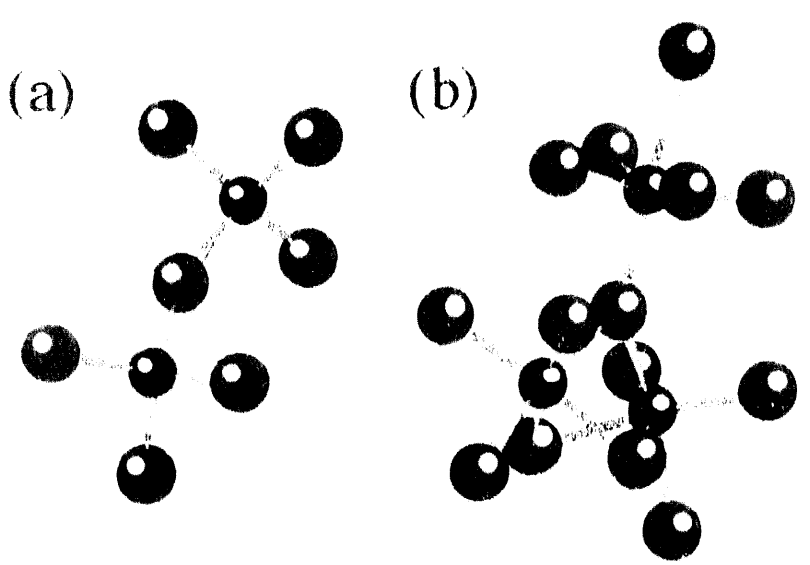

Figure 5: a) Corner-sharing SiO_4 tetrahedra in silica glass at normal density, 2.2 g/cm^3; and b) corner-sharing and edge-bonded SiO_6 octahedra in the new high-pressure phase of silica at a density of 4.28 g/cm^3.

§4 Structural and Dynamical Correlations in Orientationally Disordered Solid C_{60}

Since the breakthrough in the synthesis of C_{60} and the discovery of superconductivity in K_3C_{60} and Rb_3C_{60}, there has been considerable interest in the chemical and physical properties of these molecular forms of carbon. Using the tight-binding-molecular-dynamics method, we have investigated inter- and intra-molecular phonon dispersions and densities of states (DOS) of orientationally ordered and disordered solid C_{60}. Both inter-molecular and intra-molecular phonons show strong dispersions. Inter-molecular phonon DOS extends up to 7.6 meV and shows libron peaks at 2.3 meV and 3.7 meV. Orientational disorder softens libron modes. Intra-molecular phonons below 70 meV also show significant dispersion. The calculated phonon spectra agree very well with recent inelastic neutron scattering experiments. Under pressure, the orientational potential stiffens causing the libron frequency to increase at a rate of 0.4 cm^{-1}/kbar. Most Raman and infra-red active modes show strong dependence on pressure that are in good agreement with experiments.

Recently a new form of carbon, called graphitic tubule, has been discovered. Owing to the crystalline perfection, one dimensional nature, and various possible helical structures, graphitic tubules are expected to exhibit unusual mechanical, electronic, and optical properties. Realistic simulations of graphitic tubules require large system sizes which are tractable only with the tight-binding molecular dynamics method implemented on parallel supercomputers. Using this approach on the Touchstone Delta machine, we are investigating the relationship between structural and mechanical properties of graphitic tubules.

§5 Parallel Quantum Dynamics Simulations

Quantum dynamics (QD) is the sole method available for simulating the real-time dynamics of electrons and ions. The core computational kernels of the QD approach are the time-dependent Kohn-Sham equation in the density-functional formalism and Poisson's equation for the long-range electron-electron interaction. Parallel algorithms have been developed to implement these kernels on SIMD machines. The Kohn-Sham equation is solved by reducing large tridiagonal matrices to direct sums of 2x2 matrices which can be handled analytically. The solution to Poisson's equation is obtained by the dynamical-simulated-annealing approach. Both algorithms are scalable and require only nearest-neighbor communications. On MasPar's 8,192-node machine, the solution to Kohn-Sham and Poisson's equations achieve 64% (479 Mflops) and 61% (460 Mflops) of the theoretical peak performance, respectively. The QD approach has been used to investigate electron transport in disordered materials.

§6 Work in Progress

Structural, Dynamical, and Mechanical Properties of Nanophase Materials

Nanocrystalline metals and ceramics and nanoglasses with unique electrical, magnetic, and mechanical properties have been synthesized by in-situ consolidation of nanometer size atom clusters under high vacuum conditions. We are investigating the relationship between the microscopic

structure, atomic diffusion, and mechanical behavior as influenced by environment and extreme physical conditions of high temperatures, pressures, and loading rates in nanostructured Si_3N_4, SiC, TiO_2, and Al_2O_3. Considering the technological importance of nanophase ceramics and the enormity of these atomistic simulations, this is indeed a "Grand Challenge" project.

Fracture of Porous Glasses

From the technological standpoint, fracture is one of the most important material-specific issues concerning porous materials. Molecular-dynamics simulations are being performed on the Touchstone Delta machine to investigate fracture toughness, dynamics of crack propagation, and critical exponents for the width of a crack as a function of its length in porous materials. Nanoindentor simulations will be performed to study ductility and plastic deformation. Local internal stresses and hot spots, which are responsible for mechanical failure, will be investigated.

Simulations of Silicates, Aluminosilicates, and Zeolites

We are developing a new simulation approach which includes dynamic charge transfer resulting from changes in the local environment. With this technique, structural and dynamical correlations and thermodynamic and mechanical properties of silicates and aluminosilicates will be investigated. Simulations will also be performed to determine equilibrium interparticle separations, bond-angle distributions, the size distribution of pores, phonon densities-of-states, and mechanical properties of zeolites as a function of Si/Al ratio. Diffusion mechanisms for atoms and molecules in zeolite networks will be investigated.

§7 DOE Supported Publications, Invited Talks at Major Conferences, and Abstracts

Publications (1992-1993)

1. Structure of Rings in Vitreous SiO_2
   J. P. Rino, I. Ebbsjö, R. K. Kalia, A. Nakano, and P. Vashishta,
   Phys. Rev. B 47, 3053 (1993).

2. Structural Correlations in Porous Silica: Molecular Dynamics Simulation on a Parallel Computer
   A. Nakano, L. Bi, R. K. Kalia, and P. Vashishta,
   Phys. Rev. Letters 71, 85 (1993).

3. Structural Transformation, Medium Range Order and Dynamical Behavior of SiO_2 Glass at High Pressures
   W. Jin, R. K. Kalia, P. Vashishta, and J. P. Rino,
   Phys. Rev. Letters, in press.

4. Phonon dispersion and density of states of solid C_{60}
   J. Yu, R. K. Kalia, and P. Vashishta,
   Applied Physics Letters, in press.

5. Computer Simulation of Network Glasses and Molecular Dynamics Algorithm on SIMD and MIMD Machines
   P. Vashishta, D. L. Greenwell, R. K. Kalia, and A. Nakano,
   in Recent Progress in Many-Body Theories, Vol. 3, eds. T. L. Ainworth, C. E. Campbell, and B. E. Clements, E. Krotsceck (Plenum, New York, 1992), p. 481.

6. Achievements in Solid State Physics and Density Functional Theory
   M. H. Kalos, and P. Vashishta,
   in Recent Progress in Many-Body Theories, Vol. 3, eds. T. L. Ainworth, C. E. Campbell, and B. E. Clements, E. Krotsceck (Plenum, New York, 1992), p. 493.

7. Parallel Multiple-Time Step-Molecular Dynamics with Three-Body Interaction
   A. Nakano, P. Vashishta, and R. K. Kalia,
   Computer Physics Communications, in press.

8. Structural and Dynamical Correlations in Glasses
   W. Jin, J. P. Rino, P. Vashishta , R. K. Kalia, and A. Nakano,
   in Strongly Coupled Plasma Physics, edited by H. M. Van Horn and S. Ichirmaru (University of Rochester Press, Rochester, 1993), in press.

9. Molecular Dynamics Simulation of Network Glasses and Algorithms on Parallel (SIMD & MIMD) Architectures
   P. Vashishta, R. K. Kalia, W. Jin, A. Nakano, and D. L. Greenwell,
   in Computer Aided Innovation of New Materials II, edited by M. Doyama et al. (North Holland, Amsterdam, 1993), p. 235.

10. Atomistic Simulations on Parallel Architectures
    R. K. Kalia, W. Jin, S. de Leeuw, A. Nakano, and P. Vashishta,
    Int. J. Quantum Chemistry, in press.

11. Dynamical Structure Factor and Vibrational Normal Modes of SiO_2 Glass
W. Jin, R. K. Kalia, and P. Vashishta,
Mat. Res. Soc. Symp. Proc. 291, 343 (1993).

12. Dynamical Structure Factor and Vibrational Properties of SiO_2 Glass
W. Jin, R. K. Kalia, P. Vashishta, and J. P. Rino,
Phys. Rev. B, in press.

13. Classical and Quantum Simulations for Large Systems on Parallel Computers
P. Vashishta, R. K. Kalia, and J. Yu,
Mat. Res. Soc. Symp. Proc. 291, 3 (1993).

14. Structure, Fragmentation, and Phonons in Silicon Microclusters
Wei Li, Rajiv K. Kalia, and Priya Vashishta,
Mat. Res. Soc. Symp. Proc. 293, (1993).

Invited Talks at Major Conferences (1992-1993)

1. *Structural and Dynamical Correlations in Glasses*
"International Conference on Physics of Strongly Coupled Plasmas",
Rochester, New York, August 17-21, 1992.

2. *Molecular Dynamics Simulation of Strongly Covalent Systems with Coulomb Interactions*
"International Conference on Computational Physics for Condensed Matter Phenomena", Tokyo, Japan, September 19-21, 1992.

3. *Molecular Dynamics Simulation of Network Glasses & MD Algorithm on Parallel Computers*
"Second International Conference on Computer Applications to Materials and Molecular Science and Engineering", Yokohama, Japan, September 22-25, 1992.

4. *Covalent Glasses at Large Positive and Negative Pressures - A Molecular Dynamics Study*
"New Developments of Computer Based Design of Functional materials",
Osaka, Japan, September 29-30, 1992.

5. *Molecular Dynamics Simulation of Covalent Glasses*
"Southeastern Section Section American Physical Society Meeting",
Oak Ridge, Tennessee, November 12-14, 1992.

6. *Classical and Quantum Simulations for Large Systems on Parallel Computers*
"Theory and Modeling" Symposium at the Annual Materials Research Society Meeting, Boston, November 29-December 4, 1992.

7. *Structure and Dynamics of Network Glasses at Very large Positive and Negative Pressures - A Molecular Dynamics Study*
"Solid State Ionics" Symposium at the Annual Materials Research Society Meeting, Boston, November 29-December 4, 1992.

8. *Computational approach to nanotechnology on parallel architectures*
"Mardi Gras '93, Concurrent Computing Conference in the Physical Sciences",
Baton Rouge, Louisiana, February 18-20, 1993.

9. *Covalent Glasses at Very Large Positive and Negative Pressures - A Molecular Dynamics Study*
"The Metallurgical Society of America", Denver, Colorado, February 21-25, 1993.

10. *Structure and Dynamics of SiO_2 at Very Large Positive and Negative Pressures*
"American Chemical Society Meeting", Denver, Colorado, March 28-April 2, 1993.

11. *Molecular Dynamics of Silica Under Very Large Positive and Negative Pressures on Parallel Computers*
"High Performance Computing - 1993 Simulation MultiConference" ,
Washington DC, March 29-April 1, 1993.

Conference organizers provided most of the travel and other expenses.

Conference Presentations and Abstracts (1992-1993)

1. Structural and Dynamical Correlations in Glasses
W. Jin, J. P. Rino, P. Vashishta, R. K. Kalia, and A. Nakano,
International Conference on the Physics of Strongly Coupled Plasmas, Rochester, New York, August 17-21, 1992.

2. Dynamical Structure Factor and Vibrational Normal Modes of SiO_2 Glass
W. Jin, S. de Leeuw, R. K. Kalia, and P. Vashishta,
MRS Fall 92 Abstracts, p. 490.

3. Structural and Dynamical Correlations in Stishovite and High Density Vitreous Silica
W. Jin, R. K. Kalia, and P. Vashishta,
MRS Fall 92 Abstracts, p. 585.

4. Classical and Quantum Simulations for Large Systems on Parallel Computers
P. Vashishta, R. K. Kalia, and J. Yu,
MRS Fall 92 Abstracts, p. 475.

5. Structure, Fragmentation, and Phonons in Silicon Microclusters
Wei Li, Rajiv K. Kalia, and Priya Vashishta,
MRS Fall 92 Abstracts, p. 593.

6. Structure and Dynamics of Network Glasses at Very large Positive and Negative Pressures - A Molecular Dynamics Study
P. Vashishta and R. K. Kalia,
MRS Fall 92 Abstracts, p. 584.

7. Molecular Dynamics Simulation of Aerogel Silica on Parallel Computers
A. Nakano, R. K. Kalia, and P. Vashishta,
MRS Fall 92 Abstracts, p. 585.

8. Covalent Glasses at Large Positive and Negative Pressures: A Molecular Dynamics Study
P. Vashishta, R. K. Kalia, A. Nakano, and W. Jin,
1993 Minerals, Metals and Materials Society Annual Meeting, Denver, CO, February 21 - 25, 1993, Abstracts, p. B35.

9. Structure and Dynamics of SiO_2 at Very Large Positive and Negative Pressures
P. Vashishta, W. Jin, R. K. Kalia, and A. Nakano,
1993 American Chemical Society National Meeting, Denver, CO, March 28 - April 2, 1993, Program, p. 95.

10. Molecular Dynamics of Silica Under Very Large Positive and Negative Pressures on Parallel Computers
    P. Vashishta, R. Kalia, W. Jin, and A. Nakano,
    1993 Simulation MultiConference, Washington D.C., March 29 - April 1, 1993.

11. Dynamical Structure Factor and Vibrational Excitations of SiO_2 Glass
    W. Jin, R. K. Kalia, and P. Vashishta,
    Bull. Am. Phys. Soc. 38, 574 (1993).

12. Structural Transformation, Intermediate-Range Order and Dynamical Behavior of SiO_2 Glass at High Pressures
    W. Jin, R. K. Kalia, and P. Vashishta,
    Bull. Am. Phys. Soc. 38, 675 (1993).

13. Structural Correlations in Porous Silica: Parallel Molecular Dynamics Simulations
    A. Nakano, R. K. Kalia, and P. Vashishta,
    Bull. Am. Phys. Soc. 38, 673 (1993).

14. Phonon Dispersion and Density of States of Solid C_{60}
    J. Yu, R. K. Kalia, and P. Vashishta,
    Bull. Am. Phys. Soc. 38, 441 (1993).

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